SPECTROSCOPY AND PHOTOCHEMISTRY OF POLYNUCLEAR METAL COMPLEXES

Thesis by

Andrew William Maverick

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1982

(Submitted 4 September 1981)

Acknowledgments

First of all, I thank Harry Gray for his advice and encouragement during my stay at Caltech. I hope some of his enthusiasm for science — and perhaps an idea or two — will rub off. Particularly memorable were a "helpful discussion" and his (admittedly second-hand) statement that, if one's current research project fails for six months running, one should get a new one.

My advisor-away-from-home was Jack Dunitz. I thank him for his insight and his generosity with time and facilities, even though he seems not to want his name on any of my papers.

Thanks go to a number of friends at Caltech. Among them are Jan and Carol, fellow aspiring buckaroos; Terry, who is looking for a few good R factors; and Keith, a constant companion on the hikes we didn't take. Without experimental assistance from Jan and Doug there would be too many electrons and not enough numbers in this thesis. Also instrumental in one aspect or another of my mental deterioration were Jay (one break per person), Dan, Steves R & M, Yo, Ann, Vince, the 332 for Lunch Bunch, people who don't make puns unless made pun of, and sundry geologists (the only kind?). And, in absentia, Pz, Daivd, Vanessa, John, Paul and Wyman. Good luck to Tom and Mike, who took one or two metal atoms out while I wasn't looking -- and are now trying to get them back in.

The NSF and the Standard Oil Co. (Ohio) enabled me to live the life o' Riley (oh really?) here. As a result, the average standard of living will increase in both Pasadena and St. Louis on my departure.

Finally, I wouldn't have made it very far without my family. My father was always ready with "How's your work going?" Credit specifically for Appendix II and generally for crystallographic and chemical expertise must go to my mother. But I found inspiration and love from both of them, and from Mary and Vance, and this thesis is dedicated to them.

ABSTRACT

The photochemical and spectroscopic properties of two classes of polynuclear metal complexes have been studied.

Molybdenum and Tungsten Cluster Halides: The cubic ions $Mo_6Cl_{14}^{2-}$, $Mo_6Br_{14}^{2-}$, and $W_6Cl_{14}^{2-}$ are luminescent, with lifetimes approaching 200 μs in solution at room temperature. The luminescent excited state of $Mo_6Cl_{14}^{2-}$ is probably associated with a transition localized on the central Mo_6 core. Both this excited state and the corresponding ground state undergo facile one electron oxidation. These features make the cluster ions attractive for experiments in photochemical energy storage. Also discussed is evidence from magnetic and spectroscopic studies bearing on the electronic structures of the cluster ions.

Rhodium Isocyanide Complexes: Various thermal and photochemical reactions in the system $Rh_2b_4^{2+}$ - $Rh_4b_8^{6+}$ - $Rh_2b_4^{4+}$ (b = 1,3-diisocyanopropane) have been examined. The possibility of photocatalytic hydrogen production sensitized by $Rh_2b_4^{2+}$ and $Rh_4b_8^{6+}$, previously shown to produce H_2 stoichiometrically on irradiation in strongly acidic solution, was explored. Experiments were also conducted with $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-diisocyano-2,5-dimethylhexane) in the hopes of accomplishing similar energy storage reactions. The equilibria in acidic aqueous solution involving these species as well as oligomers of intermediate oxidation state were also studied. Kinetic studies of the reduction of $Rh_2b_4^{4+}$ by H_2 and of thermal and photochemical oxidation of $Rh_4b_8^{6+}$ by O_2 were inconclusive.

Appendix I: The magnetic susceptibility of $(Bu_4N)_2Mo_6Cl_{14}$ is ca. -650×10^{-6} emu mol^{-1} at room temperature, and increases less than 10% as the temperature is lowered to 2 K.

Appendix II: The crystal structure of $[Rh_2(TMB)_4Cl_2](PF_6)_2$ is briefly reported and compared with those of a number of polynuclear isocyanide complexes in the literature.

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

The study of inorganic photochemistry has been a popular one for several reasons. First, coordination compounds are often intensely colored; thus, in contrast to the relatively high energies required for excitation of organic molecules, a variety of reactions are accessible to visible light for inorganic chromophores. Second, the stability of metal complexes in multiple oxidation states has greatly encouraged the study of redox reactions in their ground and excited states. And finally, photochemistry is a logical part of a serious study of electronic structure and chemical bonding in any type of molecule. Here the advances made in the last several decades concerning the electronic structure of metal complexes have gone hand in hand with explorations of their photochemical and photophysical properties.

Early progress in photochemical studies of inorganic compounds has been reviewed by Balzani and Carassiti.[1] The majority of the systems investigated up to 1970 were aqueous solutions of octahedral complexes, particularly of the thermally substitution-inert Co(III) and Cr(III) ions. The principal modes of photochemical activity were ligand substitution, isomerizaton and redox processes. The first two were rationalized in terms of ligand-field excited states, such as those reached by $d\pi \rightarrow d\sigma^*$ transitions, which destabilized metal-ligand bonds. The redox processes were usually associated with charge transfer excited states, required light of relatively high energy, and often involved the formation of ligand radicals or solvated electrons.

Even at the time of Balzani and Carassiti's review, however, the field had begun to expand in the direction of other types of complexes. After organometallic compounds and species containing single and multiple metal-metal bonds had been prepared and chemically characterized,

they came under photochemical scrutiny as well. The continued expansion of research in this area is documented in the review by Bock and Koerner von Gustorf[2] and in the recent book by Geoffroy and Wrighton.[3]

Thus nearly every major class of metal complex has now been subjected to photochemical study. Recently the concentration has been not so much on greater variety of chromophore as on new photochemical processes.[4] Prominent among these have been quenching and sensitization processes involving both energy and electron transfer reactions of long-lived excited states.[5] The latter category, in which an excited molecule participates in a bimolecular electron transfer reaction, is of interest for two reasons. First, it allows for the convenient study of the kinetics of highly exergonic electron transfer reactions and provides additional opportunities for the evaluation of theories of electron transfer. Second, sensitized redox reactions are potentially valuable routes to catalytic redox reactions, with possible applications to chemical synthesis as well as photochemical energy storage.

The storage of light energy in chemical form has been a popular goal for research in several areas of photochemistry. Although photovoltaic devices are now known that convert solar energy into electricity with high efficiency, the converted energy must be used immediately. Thus a chemical scheme, in which a high-energy material such as a fuel could be produced photochemically, would have greater commercial appeal. And as the chromophore for an efficient solar energy storage reaction must absorb light in the visible or near-infrared region of the spectrum, transition metal complexes have been intensively studied as possible sensitizers.[6]

Of the reactions that have been examined for photochemical fuel formation, by far the most appealing is the splitting of water to make hydrogen and oxygen. Most experimental attacks on the water-splitting reaction have concentrated on reducing or oxidizing water separately. Oxidizing and reducing reactions could then be combined to complete a catalytic cycle. The charge transfer photochemistry of simple metal ions seemed a logical beginning. Aqueous solutions of Fe^{2+}, for example, give off H_2 when irradiated in the ultraviolet:[7]

$$Fe^{2+} + H^+ = Fe^{3+} + 1/2\ H_2 \qquad (1)$$

The work with Fe^{2+} represents both the promise and the shortcomings of this approach: although energy is definitely stored in the reaction, completion of a cycle for water splitting is difficult because the Fe^{3+} produced is not easily reduced to Fe^{2+}. An additional drawback is the wavelengths of light necessary to cause these reactions to occur: the systems operate best with wavelengths below 300 nm, which represent only a tiny portion of the solar spectrum.

The barriers involved in generating radicals such as H and OH, postulated as intermediates in these photoredox reactions, are extremely high. Thus a large energy input in the form of light can result in the storage of only a small amount of energy. The problem of radical formation and its associated energy losses has been attacked in two ways: first, by the use of excited states sufficiently long-lived to participate in bimolecular reactions; and second, by applying knowledge concerning stable free radicals to the choice of electron transfer quenchers.

The study of metal complex excited states as oxidizing and reducing agents began with the experiments of Gafney and Adamson[8] with $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine). They showed that the luminescent excited state of $Ru(bpy)_3^{2+}$ would reduce $Co(NH_3)_5Br^{2+}$, a weak electron acceptor. This demonstration that excited states can be powerful redox agents has been the basis for many subsequent experiments. Recently a number of these, based on one-electron relays and heterogeneous catalysts for gas evolution, have been successful in accomplishing one or both halves of the water-splitting reaction.

Herein are described photochemical and spectroscopic experimnets conducted with two types of metal complex. In one group, polynuclear isocyanide complexes of rhodium, the experiments relate the stoichiometric photochemical evolution of hydrogen from $Rh_4b_8^{6+}$ (b = 1,3-diisocyanopropane) to the electron transfer reactivity of the lowest excited state of $Rh_2b_4^{2+}$. The second type, cluster halides of molybdenum and tungsten, is examined for photochemical electron transfer properties as well. Here the luminescence and ground and excited state redox properties of the $M_6X_{14}^{2-}$ ions are documented for the first time, and new experimental evidence concerning their electronic structure is presented.

CHAPTER II

HALIDE CLUSTER IONS OF MOLYBDENUM AND TUNGSTEN

A. INTRODUCTION

The halides of molybdenum(II) were first described by Blömstrand in 1859.[9] Soon afterwards the first report of the analogous tungsten compounds appeared.[10] Although various detailed reports of the chemistry of these compounds suggested (see, for example, ref. 11) that they were polynuclear, the first definite structural characterization was a crystallographic study of the salt $[Mo_6Cl_8](OH)_4.14H_2O$.[12] The high overall symmetry of the staphylonuclear[13] cluster ion is evident in Figure 1, taken from a crystal structure analysis of $(NH_4)_2Mo_6Cl_{14}.H_2O$.[14] In idealized cubic symmetry, the $Mo_6Cl_{14}^{2-}$ ion consists of an octahedron of metal atoms surrounded by eight face-bridging and six axial halides. The existence of the M_6X_8 core has been demonstrated in a number of compounds: the dihalides M_6X_{12}, for example, are isomorphous, with the central M_6X_8 unit surrounded by four bridging and two terminal halides.[15]

The dihalides of molybdenum and tungsten are normally prepared at high temperatures,[16-18] suggesting that there is a substantial barrier to formation of the hexanuclear unit from mononuclear species. Consequently, their overall thermodynamic stability is difficult to assess. However, they undergo a number of chemical transformations during which the general cluster structure is modified but not destroyed. Typical reactions for "molybdenum dichloride," the most heavily studied of the cluster systems, are outlined in Figure 2. The outer (axial) ligands are easily replaced, in aprotic solvents by addition of Ag^+ [19] or in aqueous solution by addition of OH^- or other halides.[20] These substitutions appear to occur in stages, and various intermediate products

Figure 1. Structure of $Mo_6Cl_{14}^{2-}$ (after ref. 14).

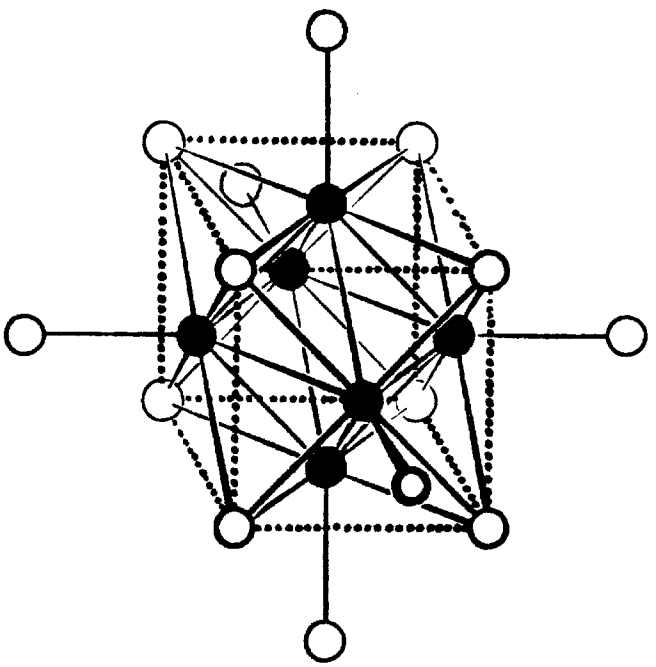
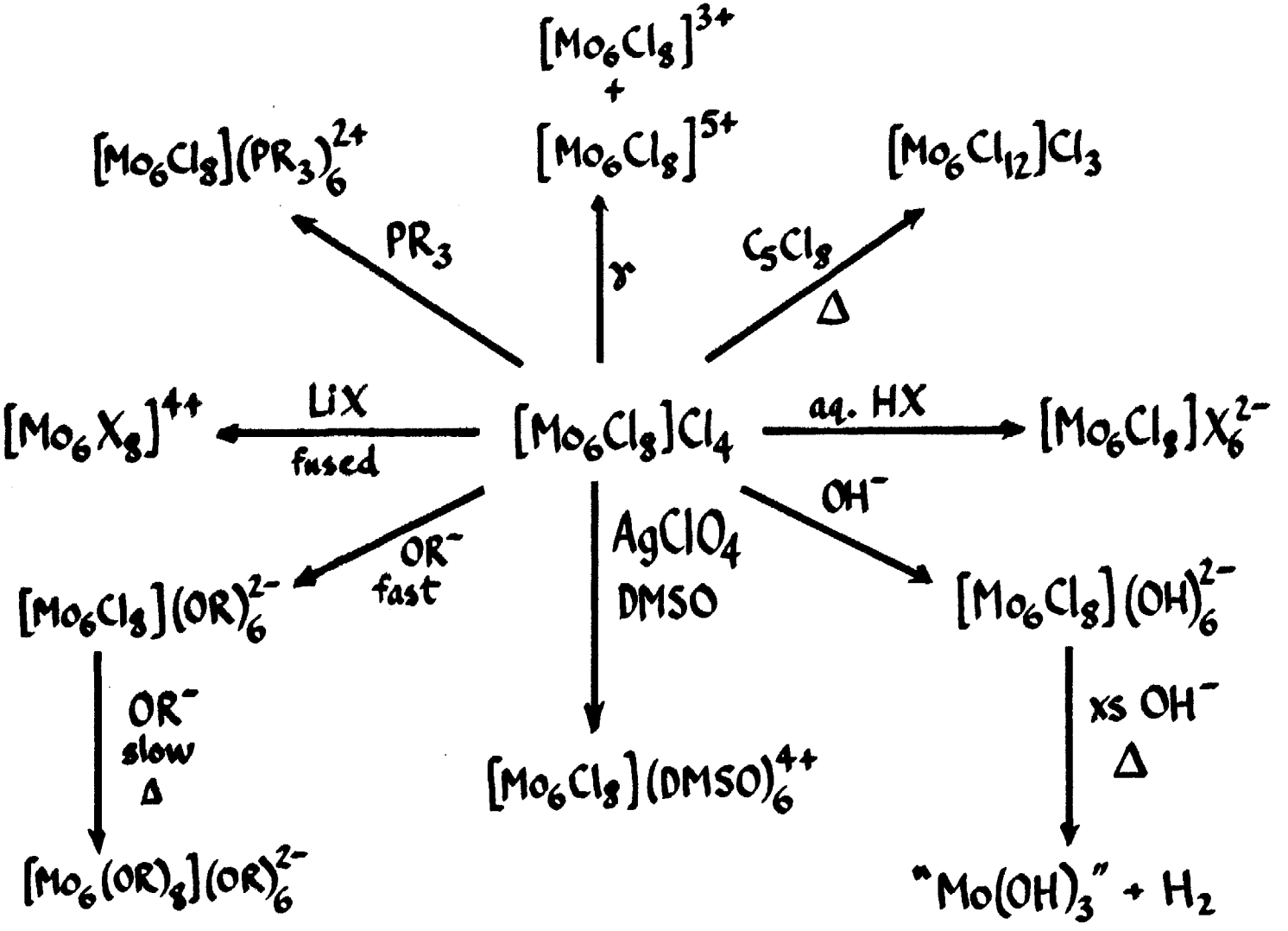


Figure 2. Reaction scheme for $[Mo_6Cl_8]Cl_4$. See text for references.


[Mo6Cl8]3+
+
[Mo6Cl8]5+
[Mo6Cl8](PR3)6 2+
[Mo6Cl12]Cl3
PR3
γ
C5Cl8
Δ
[Mo6X8]4+
LiX
fused
[Mo6Cl8]Cl4
aq. HX
[Mo6Cl8]X6 2-
OH-
OR-
fast
AgClO4
DMSO
[Mo6Cl8](OR)6 2-
[Mo6Cl8](OH)6 2-
OR-
slow
Δ
xs OH-
Δ
[Mo6Cl8](DMSO)6 4+
[Mo6(OR)8](OR)6 2-
"Mo(OH)3" + H2

can be isolated from the mixtures. Under more vigorous conditions, such as prolonged reflux in alkoxide solution[17] or fusion with lithium salts of the other halides,[21] the bridging ligands may be replaced as well.

Figure 2 also illustrates the study of redox behavior of the Mo_6Cl_8 cluster. Heating the cluster with excess of OH^- or other nucleophiles leads to fragmentation, oxidation of Mo and hydrogen production.[20] Relatively mild conditions suffice for the two electron reduction of Mo_6Cl_{12} by phosphines.[22] In this case the phosphines, coordinated to the Mo_6Cl_8 core in the products, probably assist in stabilizing the lower oxidation state. Heating with octachlorocyclopentene not only oxidized the cluster but changed its structure, giving the ion $Mo_6Cl_{12}^{3+}$ (probably with the Group V-type structure of doubly bridging halides).[23] The final example in the figure, apparently the first to show the transfer of a single electron to or from the Mo(II) cluster, is from the EPR study of Gibson and Meier.[24] Samples of gamma-irradiated Mo_6Cl_{12} gave two EPR signals, which they attributed to $Mo_6Cl_8^{3+}$ and $Mo_6Cl_8^{5+}$.

The corresponding tungsten cluster species show similar reactions,[18] although they have been less intensively studied. Two important differences have been noted, however. Oxidation of W_6Cl_{12} with octachlorocyclopentene[23] or with chlorine[25] leads to "tungsten trichloride," $[W_6Cl_{12}]Cl_6$, in contrast to the mixed Mo(II/III) species formed from Mo_6Cl_{12} (vide supra). Also, for W_6Br_{12}, two electron oxidation proceeds with Br_2 at 80-150 °C.[26] The products, various bromide and polybromide salts of $W_6Br_8^{6+}$, preserve the starting cluster core structure.[27]

Thus, although substitution reactions are well documented for these cluster species, redox processes have previously been known to occur

only with some difficulty and are often accompanied by major structural change. The present work, concentrating on the three simple ions $Mo_6Cl_{14}^{2-}$, $Mo_6Br_{14}^{2-}$ and $W_6Cl_{14}^{2-}$, constitutes a first account of their facile one electron redox processes and an examination of their spectroscopic and photochemical properties.

B. EXPERIMENTAL

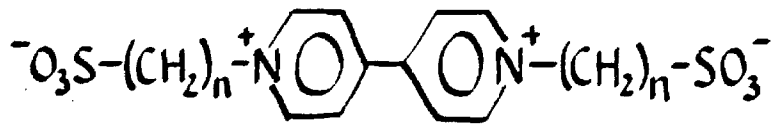
Cluster compounds. Molybdenum dichloride (Cerac Inc.) was converted to $(H_3O)_2Mo_6Cl_{14}.6H_2O$ by the method of Sheldon.[20] This salt is readily soluble in acidic aqueous media and in many polar organic solvents. But it gradually loses water and HCl on standing, to some degree even in a closed container, to give a partially hydrolyzed product that is soluble only with difficulty. Thus the potassium salt[28] was prepared by metathesis for long-term storage without degradation. A hot solution of 5 g $(H_3O)_2Mo_6Cl_{14}.6H_2O$ in 90 mL 6 M HCl was treated with a solution of 10 g KCl in 40 mL water, and bright yellow-orange needles formed on cooling. The solid was recrystallized from 125 mL 6 M HCl, rinsed with a little ice-cold 6 M HCl and dried at 100 °C. Yield 4.4 g. As heating the crystals to 100 °C. caused no change in their appearance, they are most likely anhydrous (the hexahydrate was reported by Lindner et al.[28] to lose its water at 36 °C.; thus it was probably never formed in this example). The ammonium salt,[14] also formed by metathesis, was used for measurements of spectra and extinction coefficients in aqueous solution.

Crude tungsten dichloride, as received from Varlacoid Chemical Co., was a black powder (43 g). This was heated with 800 mL 6 M HCl, kept at reflux for 2 hr., and filtered while hot. The black filter cake was discarded and the filtrate, after concentration to 100 mL on a hot plate, deposited yellow needles on cooling. This procedure was repeated twice, with smaller volumes of HCl, and ultimately afforded bright lemon-yellow needles, slightly contaminated with small brown crystals. Finally the cluster was isolated as its ammonium salt, probably a

hydrate, by metathesis with NH_4Cl in hot 6 M HCl. Yield after drying over P_2O_5 in a vacuum desiccator: 12.7 g.

All experiments in nonaqueous solutions used the tetrabutylammonium salts $(Bu_4N)_2M_6X_{14}$. The salt $(Bu_4N)_2Mo_6Br_{14}$ was prepared by the method of Sheldon,[21] starting with molybdenum dibromide (Alfa) and substituting Bu_4NCl for Et_4NCl. For the molybdenum and tungsten chloride salts the method of Hogue and McCarley[18] sufficed, with $K_2Mo_6Cl_{14}$ and $(NH_4)_2W_6Cl_{14}.xH_2O$ respectively as starting materials. The tetrabutylammonium salts, obtained originally as pale powdery precipitates from aqueous solution, were taken up in dichloromethane and the solutions dried over Na_2SO_4, filtered and allowed to evaporate in air at room temperature. Prismatic crystals, some as large as 5 mm dia., grew over a period of several days. Prominent faces of these crystals were hexagonal in outline and not noticeably dichroic, and showed parallel extinction and off-center biaxial optic axis interference figures between crossed polarizers. The crystals are probably monoclinic. Anal. $(Bu_4N)_2Mo_6Cl_{14}$, yellow-orange crystals. Calcd. for $C_{32}H_{72}N_2Mo_6Cl_{14}$: C, 24.69; H, 4.66; N, 1.80. Found: C, 24.71, 24.42; H, 4.63,4.39; N, 1.97,1.88. $(Bu_4N)_2Mo_6Br_{14}$, deep orange crystals. Calcd.: C, 17.64; H, 3.33; N, 1.285. Found: C, 17.51, 17.21; H, 3.28, 3.14; N, 1.32, 1.26. $(Bu_4N)_2W_6Cl_{14}$, lemon-yellow crystals. Calcd.: C, 18.44; H, 3.48; N, 1.34. Found: C, 18.22, 18.25; H, 3.31, 3.38; N, 1.40, 1.29.

Other reagents. Methylviologen (1,1′-dimethyl-4,4′-bipyridinium dichloride monohydrate) was purchased from Aldrich Chemical Co. and used without further purification. A sample of BSEP (1,1′-bis(2-sulfoethyl)-4,4′-bipyridinium, inner salt, $\underset{\sim}{1}$)



1, BSEP (n = 2) 2, BSPP (n = 3)

was obtained from Professor George McLendon. Additional quantities of BSEP and the homolog BSPP (1,1′-bis(3-sulfopropyl)-4,4′-bipyridinium, inner salt, 2) were prepared by a modification of the method of Le Berre and co-workers.[29] Ethenesulfonyl chloride was the principal sulfoalkylating agent in their work, but they found that 2-chloroethanesulfonyl chloride gave similar results in other cases. The same strategy was adopted here for BSEP.

A mixture of 4,4′-bipyridine dihydrate (Aldrich), 8.33 g (0.0433 mole), 10 g acetic anhydride and 40 mL glacial acetic acid was warmed, to dissolve the bipyridine and dehydrate it, and allowed to cool somewhat. To that solution was added 14.13 g (0.0866 mole) 2-chloroethanesulfonyl chloride (Eastman), and the mixture was heated to 120-130 °C., first at atmospheric pressure (45 min.) and then under aspirator vacuum (45 min.) to remove the solvent. The mixture solidified as the solvent was removed. After cooling, the dark brown, foul-smelling solid was dissolved in water, the liquid treated with charcoal and filtered, and crude BSEP precipitated from the filtrate by flooding with three times its volume of ethanol. This sequence of dissolution, charcoal treatment and reprecipitation was repeated twice more, finally affording highly reflective white microcrystalline flakes. These were recrystallized from acidified water (approx. 3 mL, and one drop conc. HCl, per g), giving colorless crystals that were collected, rinsed with

ethanol, acetone and dichloromethane, and dried in an oven at 100 °C. Yield 6.31 g (0.017 mole, 40%).

The procedure for BSPP was nearly identical but employed 3-propane sultone (3-hydroxypropanesulfonic acid, sultone; Aldrich; CAUTION! CANCER SUSPECT AGENT!) as sulfoalkylating agent.[30] As BSPP is more soluble in water than BSEP, the final recrystallization required less water and proceeded in lower yield. ^{1}H nmr for BSPP: δ 2.3 (quintet, 4H, $-CH_2-$), 2.8 (triplet, 4H, $-CH_2SO_3^-$), 4.7 (triplet, 4H, N^+-CH_2-), 8.4,9.0 (AB quartet, 8H, aromatic). Chemical shifts estimated relative to DSS.

Samples of BSEP and BSPP isolated at intermediate stages by precipitation with ethanol tend to turn blue on standing. This suggests some kind of reductive decomposition. Bird and Kuhn[31] confirm that base hydrolysis of alkylviologens yields alcohols that can sometimes act as reductants, resulting in the spontaneous development of a blue color. Conducting the final crystallization in acidified water, however, appears to inhibit the decomposition and gives colorless crystals.

Extinction coefficients for $BSEP^-$ and $BSPP^-$ were measured in 0.1 mM solutions of the viologens in 0.08 M $NaHCO_3$ - 0.08 M Na_2CO_3 using excess $Na_2S_2O_4$ as reductant. Spectra of these blue solutions were similar to that of MV^+,[32] giving by comparison $\epsilon_{595} = 8.3 \times 10^3$ M^{-1} cm^{-1} for $BSEP^-$ and $\epsilon_{600} = 1.04 \times 10^4$ M^{-1} cm^{-1} for $BSPP^-$. Solutions 1 mM in these radical ions were violet, probably reflecting dimerization of the type observed by Kosower and Cotter with MV^+;[32] but the low radical concentrations ($<10^{-5}$ M) developed in flash photolysis make dimerization unfavorable.

Tetracyanoethylene (ethenetetracarbonitrile, or TCNE; Aldrich), recrystallized from chlorobenzene and vacuum sublimed, was supplied by Daniel G. Nocera. Chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) was obtained from MCB and recrystallized from toluene before use.

Sodium 12-tungstophosphate, $Na_3PW_{12}O_{40}.10H_2O$, was prepared by the method of Wu,[33] stopping at the material he says "consists of sodium phospho-24-tungstate but is usually contaminated by traces of acid tungstates." This solid was recrystallized three times from 1 M H_2SO_4 and once from 1 M HCl, collected and air-dried. Potassium 12-tungstosilicate, $K_4SiW_{12}O_{40}.18H_2O$, was prepared following the procedure of Prados and Pope.[34] Commercial preparations are unreliable: samples of 12-tungstophosphoric acid (Apache) and 12-tungstoboric acid (Polysciences Inc.) were contaminated with large quantities of insoluble materials.

Tetrabutylammonium trifluoromethanesulfonate, Bu_4NTFMS, was prepared following Brandstrom's general procedure.[35] Trifluoromethanesulfonic acid (3M Co.) was converted to its monohydrate and distilled twice from activated charcoal under a stream of nitrogen at reduced pressure. The distillate sometimes crystallized (m.p. 34 °C.) on standing but could be remelted easily before use. A mixture of 67.9 g (0.20 mole) Bu_4NHSO_4 (Aldrich), 16.7 g (0.40 mole) NaOH and 300 mL H_2O was made slightly acidic with $HTFMS.H_2O$ (approx. 34 g, 0.2 mole) and the resulting slurry extracted with three 50 mL portions of CH_2Cl_2. The extract was dried over Na_2SO_4, decolorized with charcoal, filtered and evaporated to dryness in vacuo. The residue, a white foamy solid, was crystallized by trituration with ether in an ice-salt bath. These crystals were dissolved in a minimum of 2-propanol at ca. 30 °C. and

isolated by filtration after cooling the solution to -25 °C. The recrystallized material was washed while still cold with a little very cold ether and air-dried. Yield 63.8 g (0.16 mole).

Acetonitrile (UV) and dichloromethane were obtained from Burdick and Jackson Laboratories. For electrochemical studies the dichloromethane was used as received, and the acetonitrile was dried further by storage over activated alumina in a drybox. For spectroscopic and flash photolysis experiments these solvents were either distilled in vacuo from degassed, redistilled material stored over molecular sieves or used directly following degassing in five freeze-pump-thaw cycles. Hydrochloric acid (reagent) was diluted with an equal volume of water, treated with a small amount of $NH_2OH.HCl$ to remove chlorine,[36] and distilled under argon. The constant-boiling distillate was used for flash photolysis after freeze-pump-thaw degassing.

Instrumentation. Absorption spectra were measured on Cary 17 and 219 spectrophotometers. Emission spectra were recorded on an apparatus built at Caltech (200 W Hg(Xe) lamp, Spex Minimate excitation monochromator and 436 nm bandpass filter, Spex 0.5 m emission monochromator, Hamamatsu R955 or cooled R406 photomultiplier, and PAR model 186A lock-in amplifier) and were corrected for monochromator and photomultiplier response. Dilute solutions, with absorbances less than 0.02 at 436 nm,[37] were used for quantum yield measurements and absolute quantum yields estimated by comparison with $Ru(bpy)_3^{2+}$.[38] Stern-Volmer emission quenching experiments, using degassed solutions in standard 1 cm cells, were conducted on a Hitachi/Perkin-Elmer MPF-3 fluorescence spectrophotometer. Emission lifetimes were measured using 337 nm radiation from a

pulsed nitrogen laser (experiments performed at the University of California, Santa Barbara)[39] or the frequency-doubled output (532 nm) of a Quanta-Ray pulsed Nd:YAG laser (at Caltech). For low temperature work, samples were mounted in a Cryogenics Technology Inc. model 21 cryocooler. Sample temperatures with this apparatus were difficult to estimate but were probably 30 ± 10 K.

Microsecond flash photolysis experiments utilized an apparatus constructed at Caltech as described in ref. 40. Unless otherwise noted, kinetic data obtained with this apparatus were satisfactory over at least three half-lives of the absorbing species.

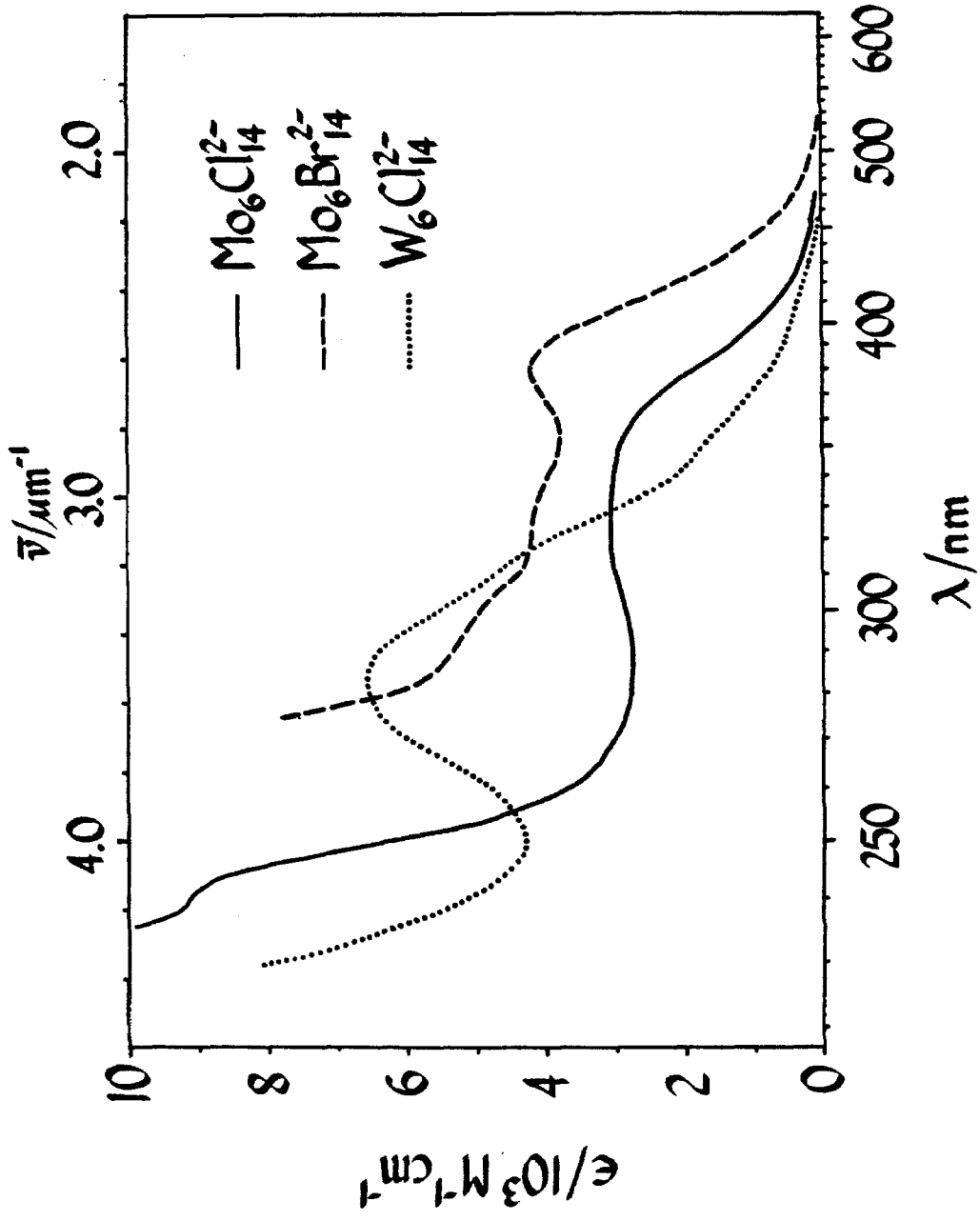
EPR spectra were recorded on a Varian E-Line Century Series spectrometer equipped with an Air Products Heli-Tran cooling system. Magnetic susceptibility measurements (see Appendix I) were made at SHE Corporation, San Diego CA 92121, using a SQUID-based susceptometer. Electrochemical measurements were made using PAR models 173, 175 and 179 electronics. For the cluster experiments, working and counter electrodes were platinum and the reference electrode was a silver - 0.1 M $AgNO_3$ (in CH_3CN) couple. Cyclic voltammetry experiments performed on BSEP and BSPP utilized a hanging mercury drop working electrode and 1 M CH_3SO_3H supporting electrolyte.

C. SPECTROSCOPY AND ELECTRONIC STRUCTURE

Efforts to understand the formation of these cluster ions in terms of electronic structure and bonding date from the crystallographic studies of Brosset.[12] He realized that the moderately (but not exceedingly!) short metal-metal bonds (2.63 Å in $Mo_6Cl_{14}^{2-}$,[14] as compared with 2.725 Å in molybdenum metal[41]) were an indication of strong bonding interactions within the cluster. It might be said without great exaggeration that Brosset's remarks place him even today in the first rank of students of the electronic structure of the M_6X_8 clusters. Occasionally new experimental information has shed some light on their bonding properties, and a number of theoretical studies have been carried out. However, the correlation among the various studies has not been good enough to provide a thorough understanding of the bonding. The present section does not make the muddy waters suddenly transparent. But the new data presented here concerning absorption and emission spectra, lifetimes, and magnetic and redox properties represent an important addition to the body of experimental knowledge. Also, some puzzling features of the theoretical treatments may be brought into substantial agreement with one another, and a unified picture painted.

Results. Solids and solutions containing the ions $Mo_6Cl_{14}^{2-}$, $Mo_6Br_{14}^{2-}$, and $W_6Cl_{14}^{2-}$ are yellow or orange in color. Their electronic absorption spectra, first recorded by Sheldon[20,21,42] for various derivatives in aqueous solutions, are dominated by intense bands in the near ultraviolet. These are illustrated in Figure 3 for tetrabutylammonium salts in acetonitrile at room temperature. Resolution in these

Figure 3. Electronic absorption spectra for the three cluster ions, as tetrabutylammonium salts in acetonitrile at room temperature.


$Mo_6Cl_{14}^{2-}$
$Mo_6Br_{14}^{2-}$
$W_6Cl_{14}^{2-}$
$\bar{\nu}/\mu m^{-1}$
4.0
3.0
2.0
λ/nm
250
300
400
500
600
$\epsilon/10^3\,M^{-1}cm^{-1}$
0
2
4
6
8
10

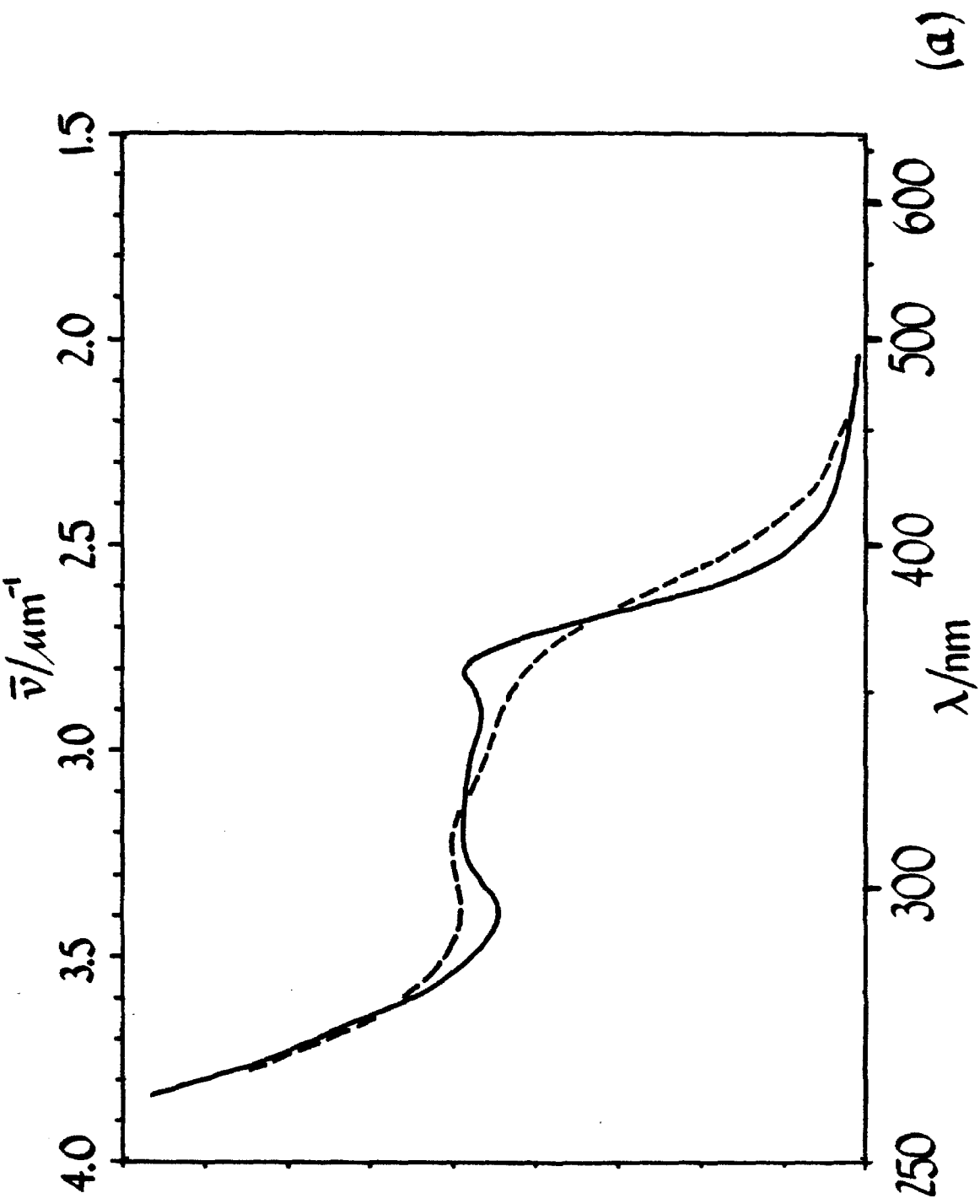
spectra is perhaps somewhat superior to that of Sheldon, but to separate the broad absorptions into individual components has only been partially possible. Additional improvement in detail is possible by examining the spectra at low temperature in poly(methyl methacrylate) films. Figure 4 allows comparisons of band intensity and position at ambient temperature and ca. 30 K.

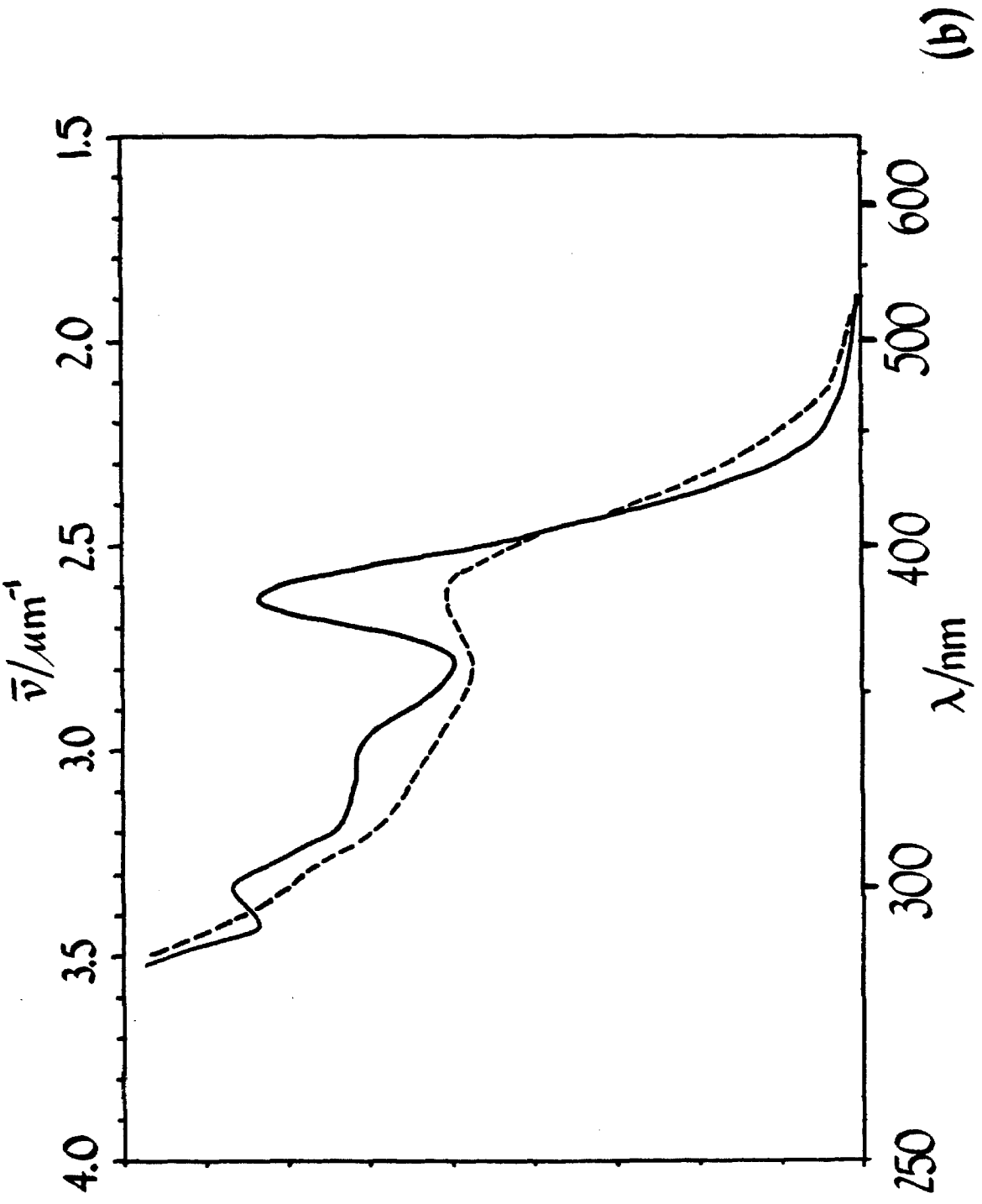
The cluster ions are luminescent, both in the solid state and in solution. Figure 5 shows corrected emission spectra for the three ions, again as tetrabutylammonium salts in acetonitrile. The spectra are plotted on a relative intensity scale, illustrating the differences in luminescence quantum yield. In contrast to the absorption spectra, whose major features are only slightly dependent on temperature, Figure 6 reveals striking changes. At low temperature, the emission bands are much narrower in all three cases, and in the $Mo_6Cl_{14}^{2-}$ and $Mo_6Br_{14}^{2-}$ spectra there is a pronounced red shift. The spectra in Figure 6 are normalized to give equal peak heights, so that the band shapes may be compared more easily. But in all cases the overall emission intensity is substantially higher at low temperature.

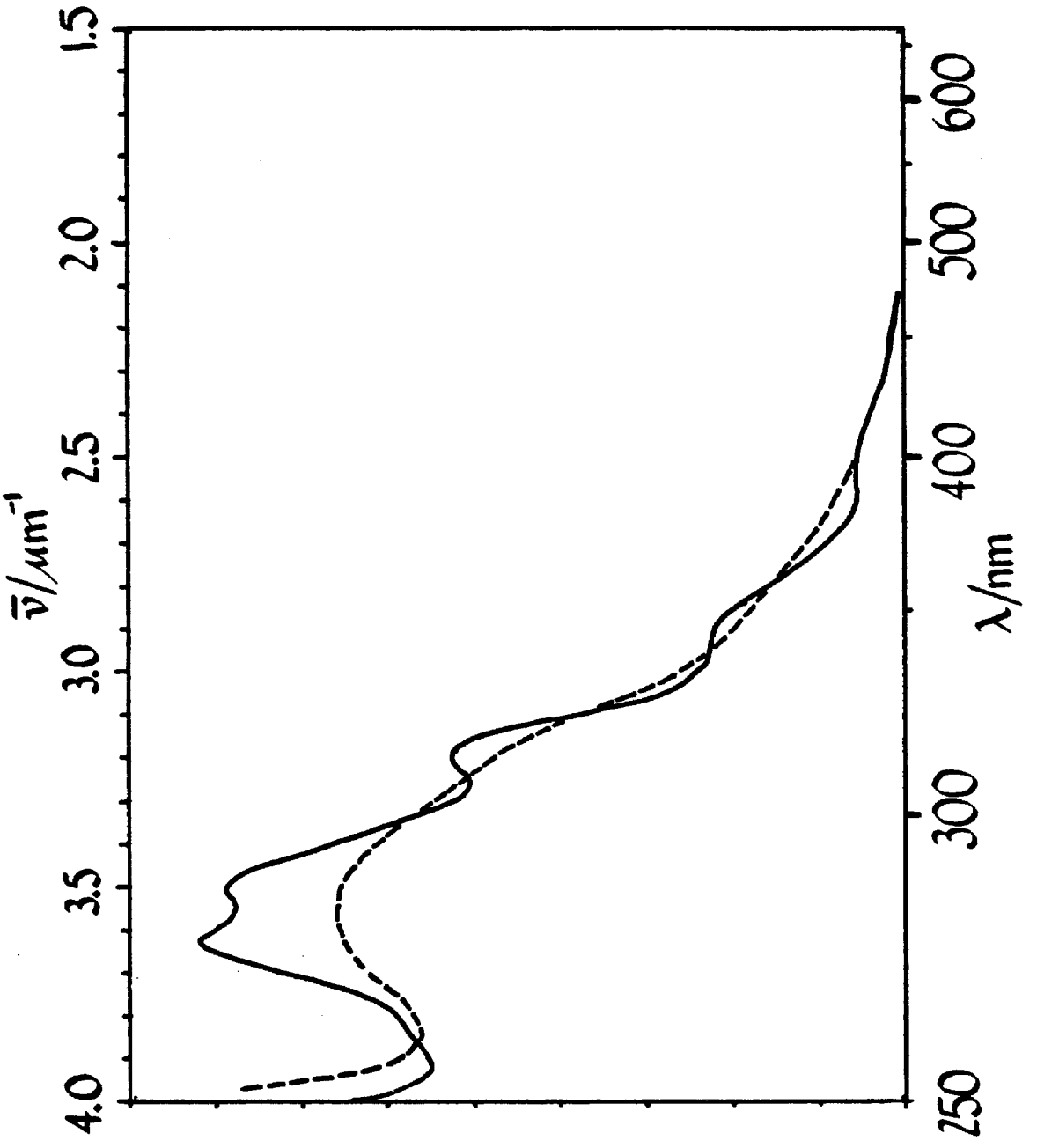
The principal spectral features for the three ions are given in Table 1.

The emission lifetimes for $Mo_6Cl_{14}^{2-}$ (Table 2) are among the longest known for any transition metal complex, approaching 200 μs in solution at room temperature. The decrease in emission lifetime on changing from acetonitrile solution to hydrochloric acid is paralleled by an approximately fivefold decrease in emission quantum yield. The emission spectra, however, are nearly identical in the two solvents.

Figure 4. Electronic absorption spectra for $(Bu_4N)_2M_6X_{14}$ in poly(methyl methacrylate) films: ------, room temperature; ———, ca. 30 K. (a) $(Bu_4N)_2Mo_6Cl_{14}$; (b) $(Bu_4N)_2Mo_6Br_{14}$; (c) $(Bu_4N)_2W_6Cl_{14}$.


(a)
$\bar{\nu}/\mu m^{-1}$
4.0
3.5
3.0
2.5
2.0
1.5
250
300
400
500
600
λ/nm


(b)
$\bar{\nu}/\mu m^{-1}$
4.0
3.5
3.0
2.5
2.0
1.5
250
300
400
500
600
λ/nm



(c)

Figure 5. Corrected emission spectra for the $M_6X_{14}^{2-}$ ions, as tetrabutylammonium salts in acetonitrile at room temperature. Excitation wavelength 436 nm.

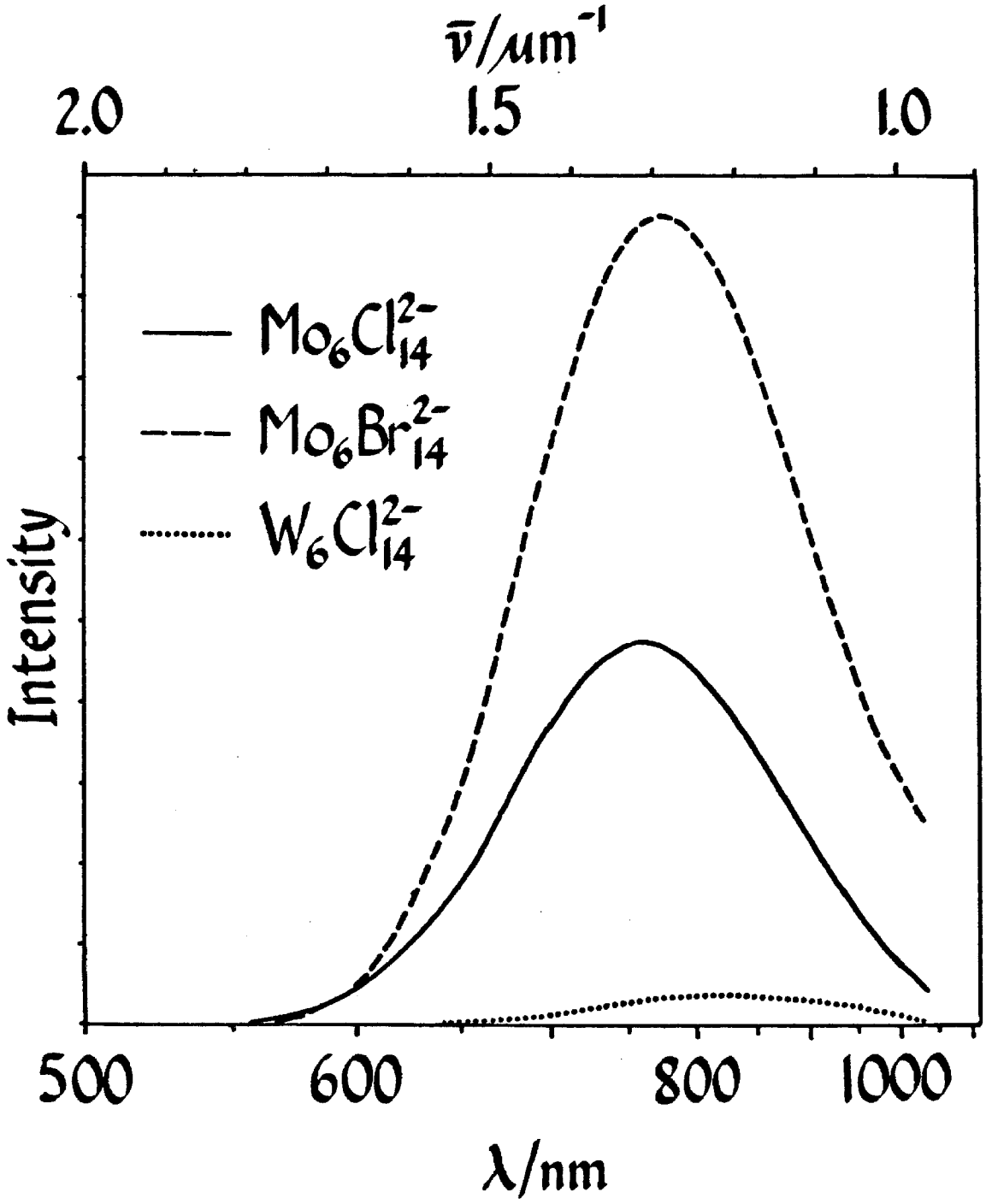
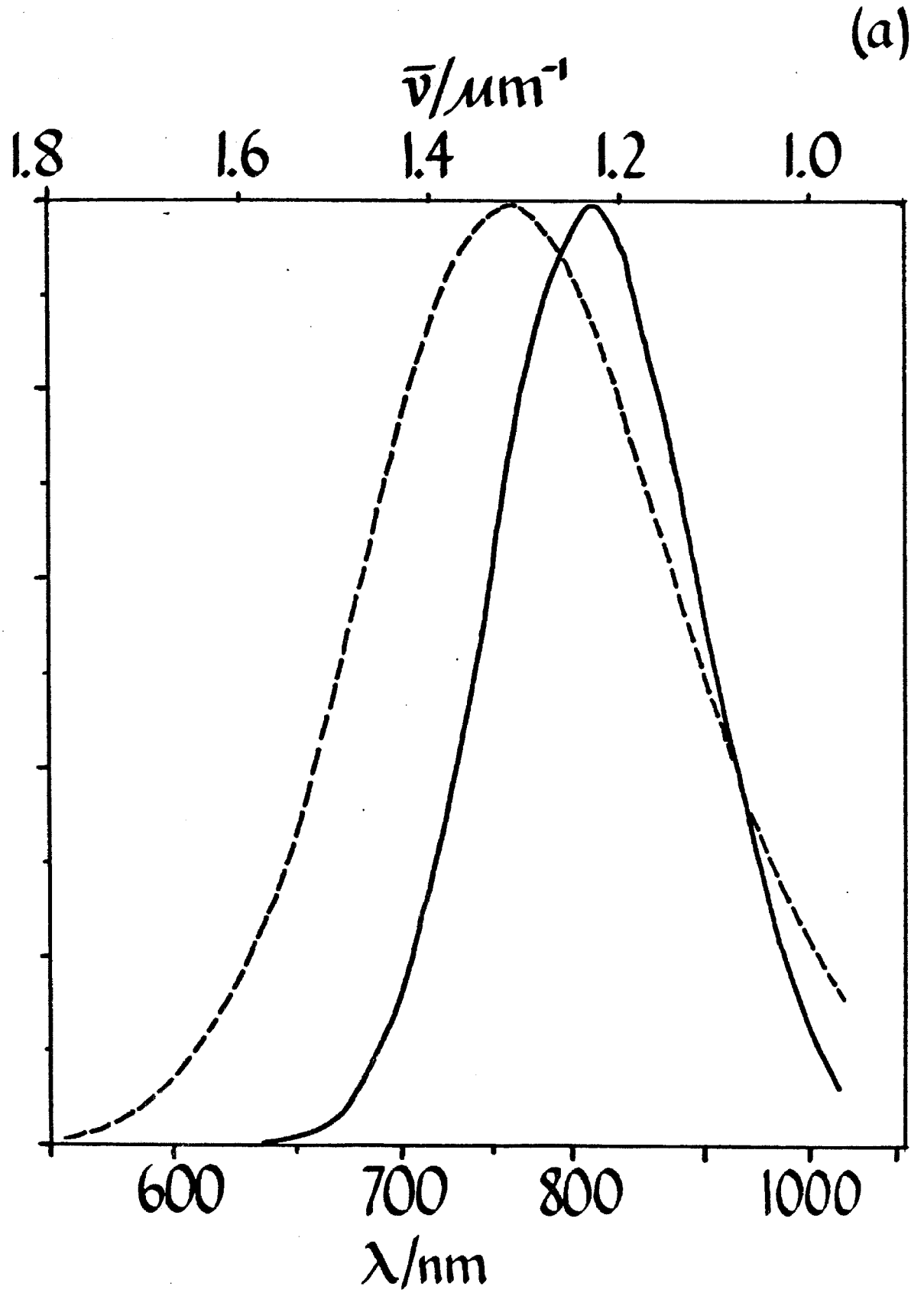
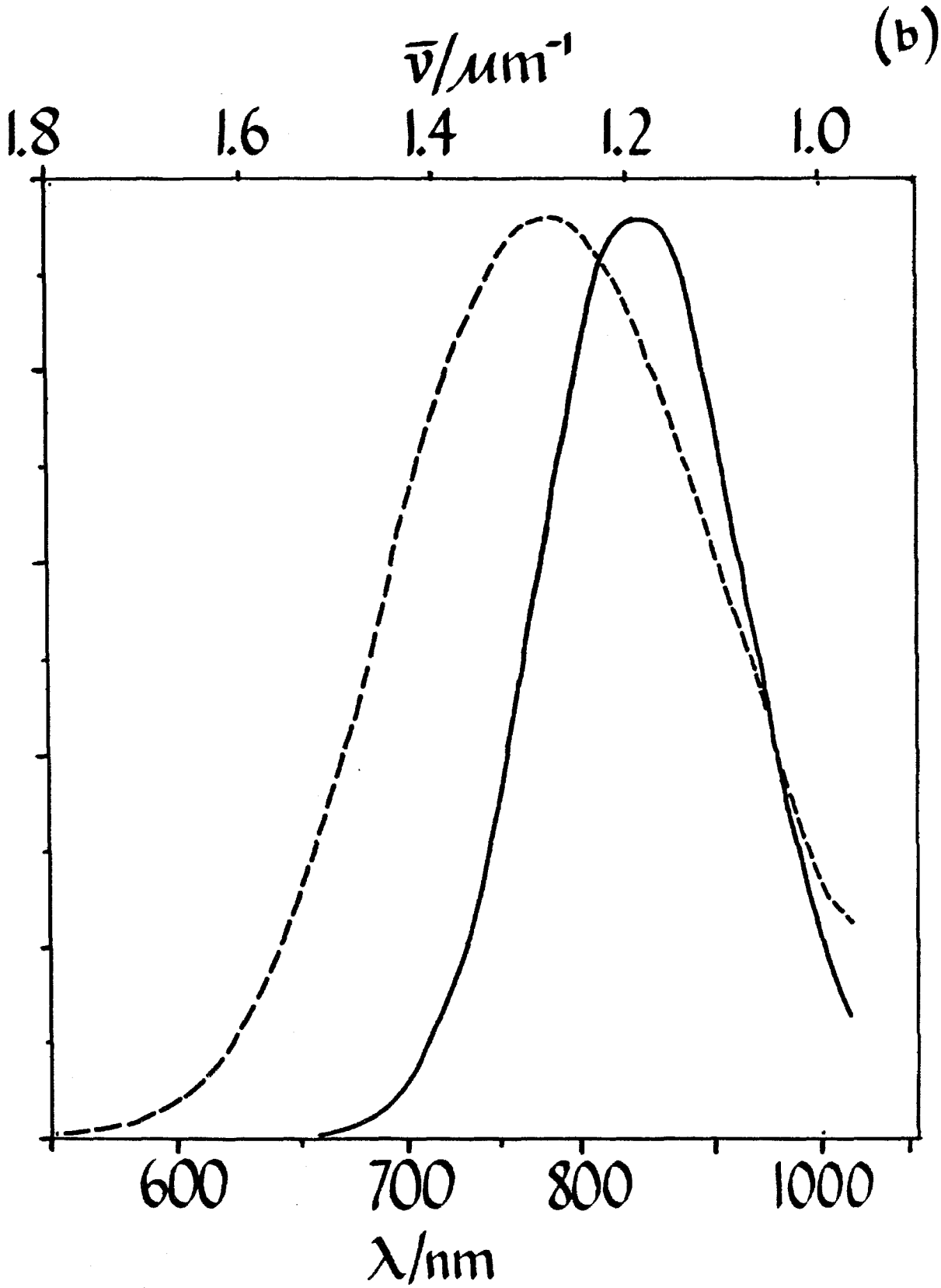

$\bar{\nu}/\mu m^{-1}$
2.0
1.5
1.0
$Mo_6Cl_{14}^{2-}$
$Mo_6Br_{14}^{2-}$
$W_6Cl_{14}^{2-}$
Intensity
500
600
800
1000
λ/nm

Figure 6. Corrected emission spectra for solid $(Bu_4N)_2M_6X_{14}$. Excitation wavelength 436 nm. ------, room temperature; ———, ca. 30 K. (a) $(Bu_4N)_2Mo_6Cl_{14}$; (b) $(Bu_4N)_2Mo_6Br_{14}$; (c) $(Bu_4N)_2W_6Cl_{14}$.


(a)
$\bar{\nu}/\mu m^{-1}$
1.8
1.6
1.4
1.2
1.0
600
700
800
1000
λ/nm


(b)
$\bar{\nu}/\mu m^{-1}$
1.8
1.6
1.4
1.2
1.0
600
700
800
1000
λ/nm

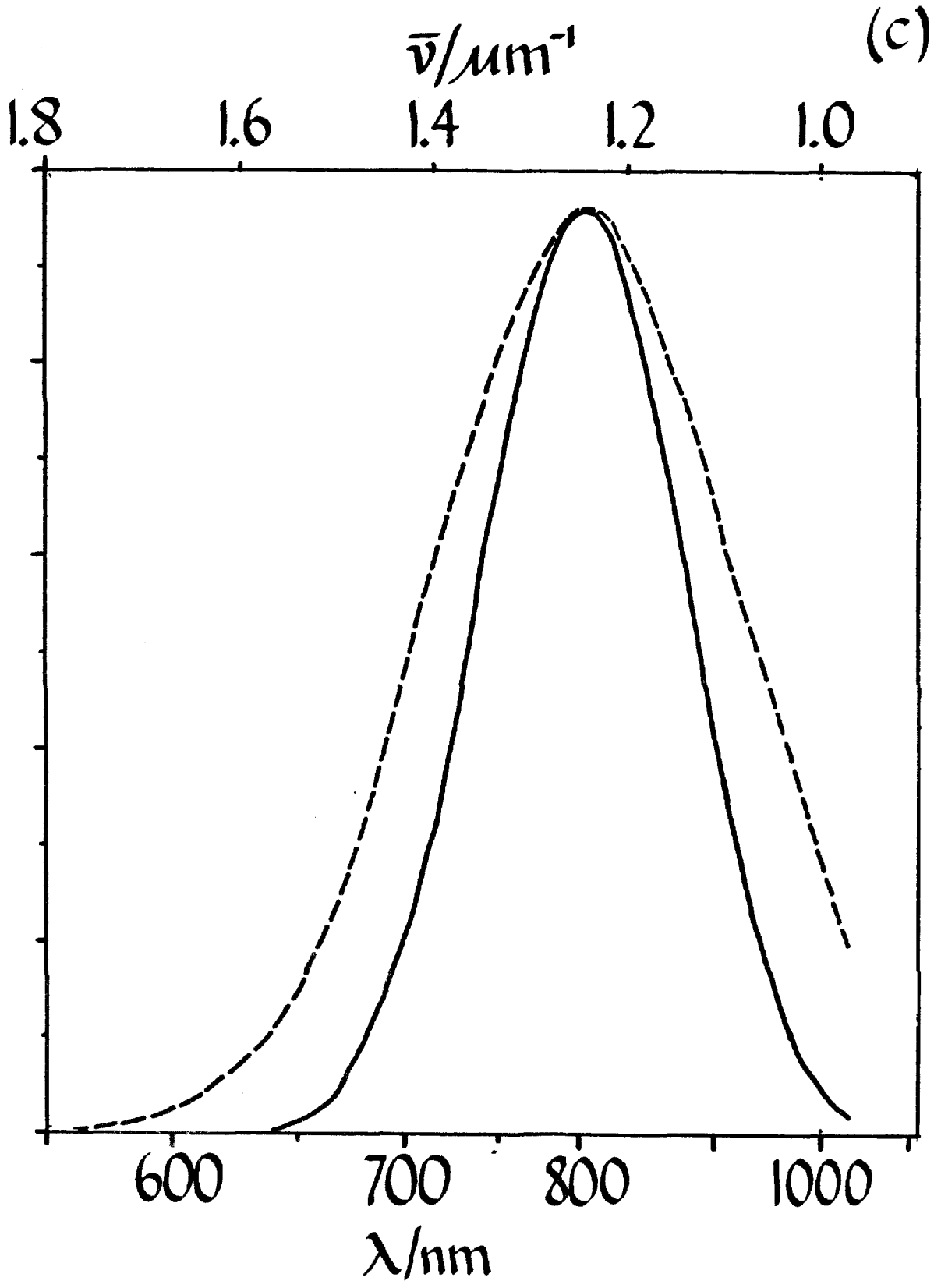

(c)
$\bar{\nu}/\mu m^{-1}$
1.8
1.6
1.4
1.2
1.0
600
700
800
1000
λ/nm

Table 1. Spectral properties of $M_6X_{14}^{2-}$ ions.

	$Mo_6Cl_{14}^{2-}$	$Mo_6Br_{14}^{2-}$	$W_6Cl_{14}^{2-}$
Absorption:			
First λ_{max}/nm (CH_3CN, 300 K)	320	380	283
$\epsilon/M^{-1}cm^{-1}$	3000	4200	6600
Emission:			
Φ (CH_3CN, 300 K)	0.044	0.097	0.003
λ_{max}/nm (solid, 300 K)	760	790	800
λ_{max}/nm (solid, 30 K)	810	840	800
FWHM/μm^{-1} (solid, 300 K)	0.39	0.40	0.37
FWHM/μm^{-1} (solid, 30 K)	0.25	0.25	0.25

Table 2. $Mo_6Cl_{14}^{2-}$ emission lifetimes.[a]

	300 K	77 K
$(H_3O)_2Mo_6Cl_{14}$ / aq. HCl + LiCl	20	80
$(Bu_4N)_2Mo_6Cl_{14}$ (solid)	120	210
/ CH_3CN	180	[b]
/ PMMA (30 K only: ca. 250)		

[a] In μs; ± 10%. [b] Not measured.

Acetonitrile solutions of $Mo_6Cl_{14}^{2-}$ also exhibit a transient absorption signal in the 450-600 nm region in flash kinetic spectroscopic experiments (Figure 7). This signal decays exponentially with a lifetime comparable to that observed in emission under the same conditions. We therefore attribute the transient signal to the luminescent excited state $Mo_6Cl_{14}^{2-*}$.

There is a relatively large energy difference between the principal absorption and emission bands in the cluster ions. In addition, the emission lifetimes are abnormally long. This combination suggested that the luminescence is likely to be associated with an electronically forbidden transition not observed directly in the major absorption bands. Accordingly I examined the low energy regions of the absorption spectra in more detail. Figure 8 depicts absorption spectra for crystals of the ions' tetrabutylammonium salts, recorded at room temperature and at ca. 30 K. The room temperature spectra are featureless, reflecting the gradual decrease in absorption associated with the intense bands in the near ultraviolet. At low temperature, however, small shoulders can be seen. The new features appear at the following wavelengths (estimated $\epsilon/M^{-1}cm^{-1}$ in parentheses): $Mo_6Cl_{14}^{2-}$, 530 (5) and 590 nm (0.5); $Mo_6Br_{14}^{2-}$, 600 nm (0.9); and $W_6Cl_{14}^{2-}$, 490 (0.6) and 550 nm (0.2). These absorption spectra offer limited resolution because the crystals fracture extensively on cooling; nevertheless, it seems clear that there are weak absorptions at relatively low energy in all three cluster ions in addition to the intense bands in the near ultraviolet. It is likely that some of these low energy transitions are associated directly with the ions' luminescent excited states. In agreement with this

Figure 7. Transient difference spectra for $(Bu_4N)_2Mo_6Cl_{14}$ in acetonitrile, 200 and 500 μs after the flash.

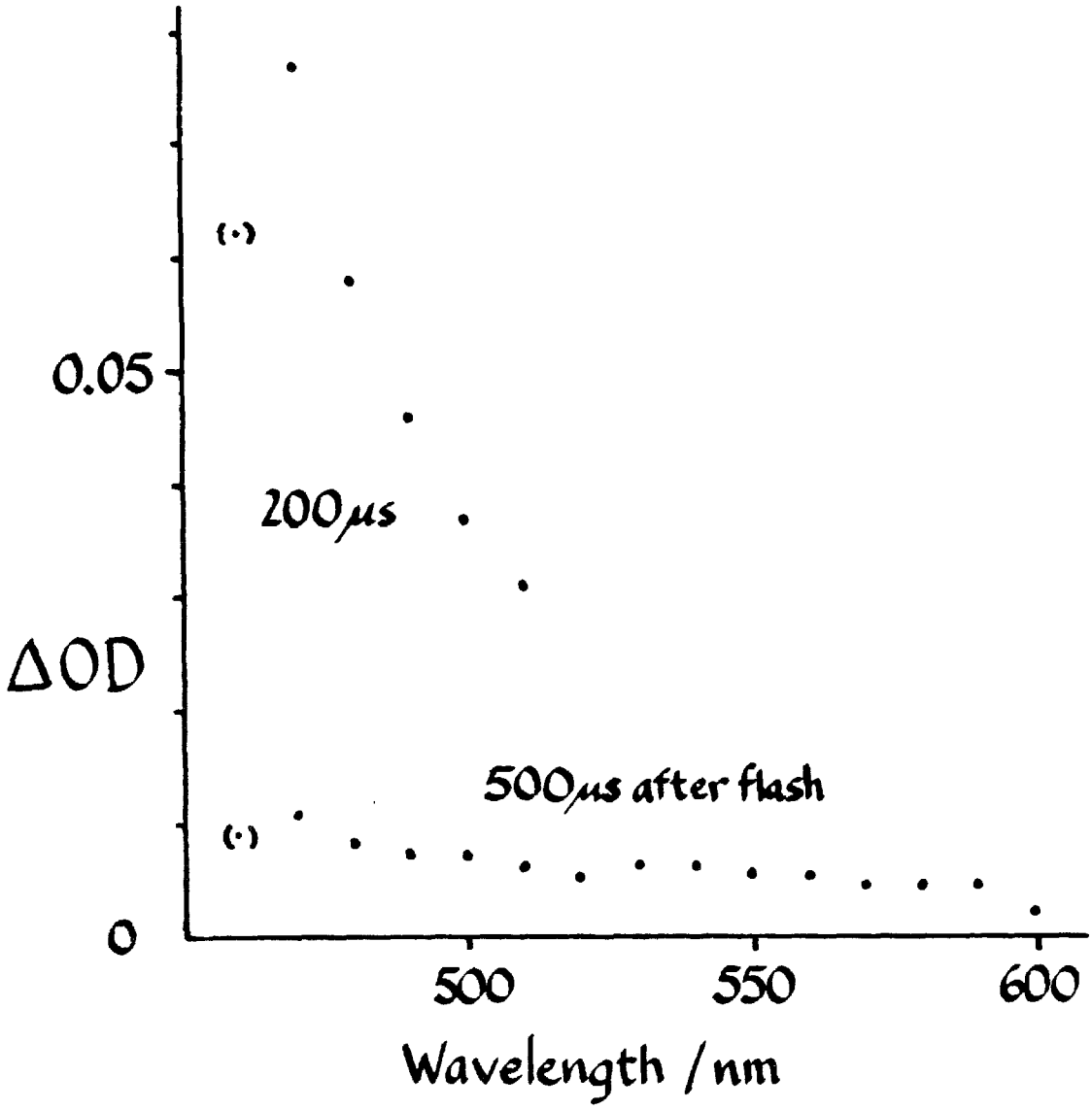
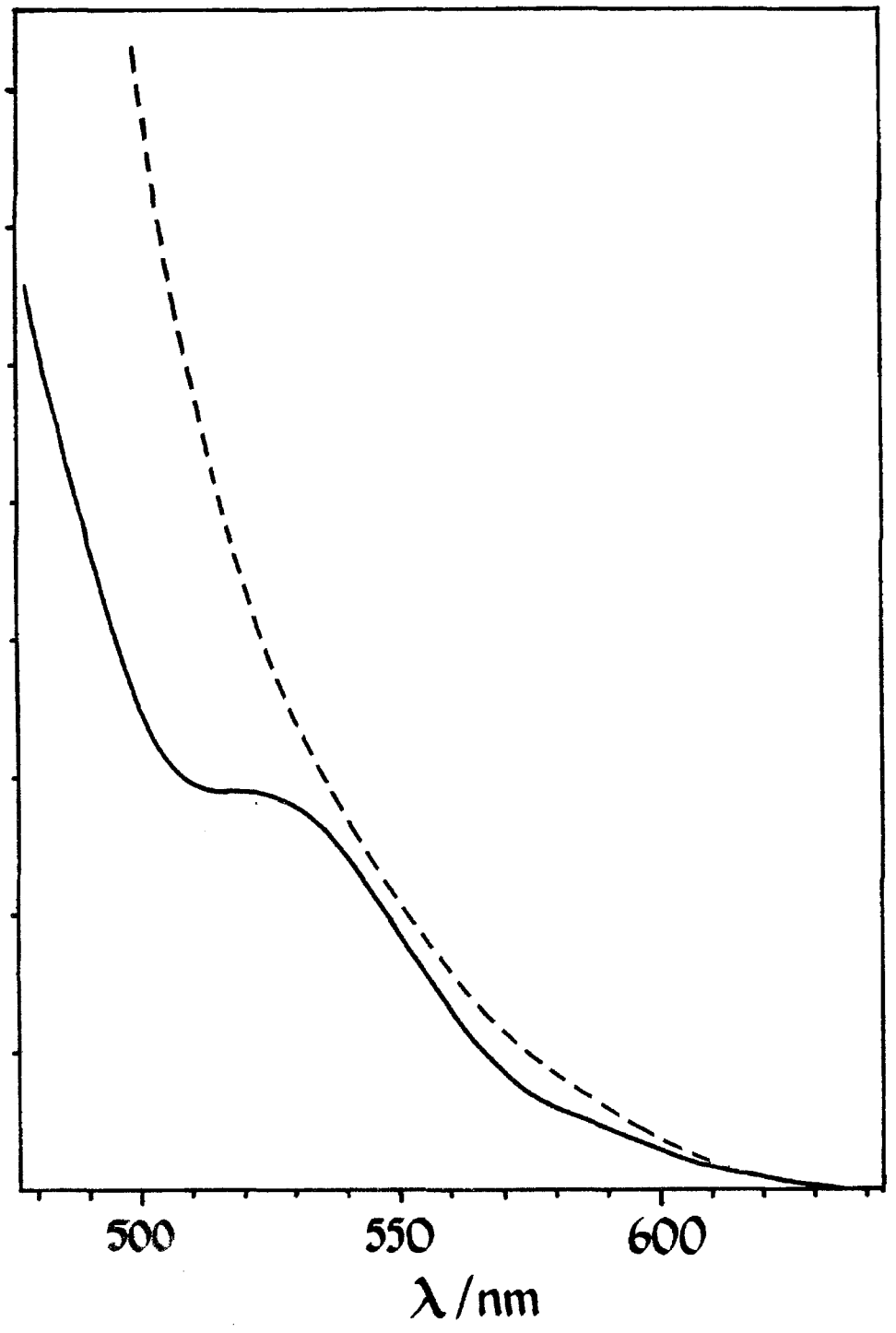
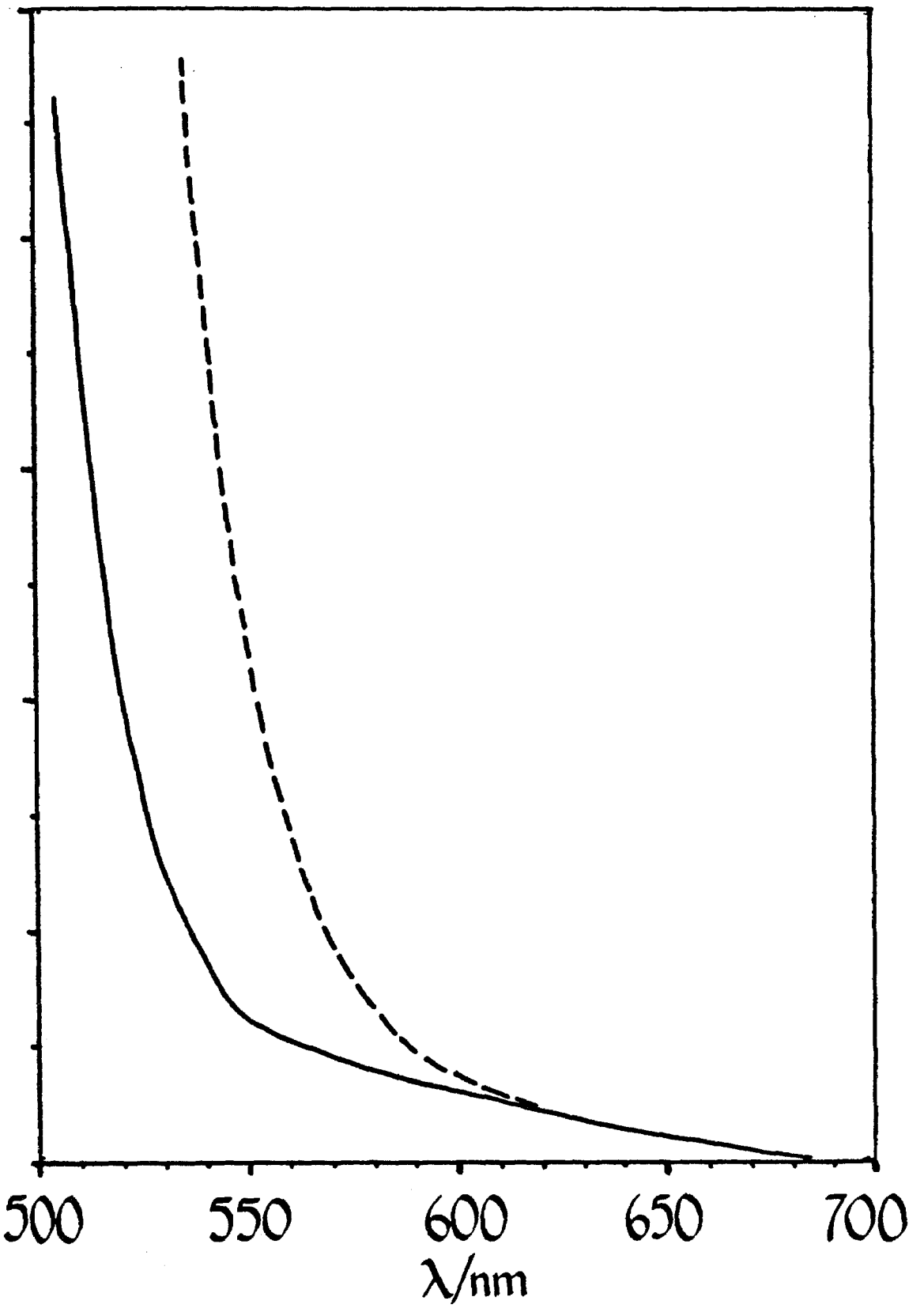

0.05
ΔOD
0
200μs
500μs after flash
500
550
600
Wavelength / nm

Figure 8. Absorption spectra for thick crystals of $(Bu_4N)_2M_6X_{14}$. ------, room temperature; ———, ca. 30 K. (a) $(Bu_4N)_2Mo_6Cl_{14}$; (b) $(Bu_4N)_2Mo_6Br_{14}$; (c) $(Bu_4N)_2W_6Cl_{14}$.

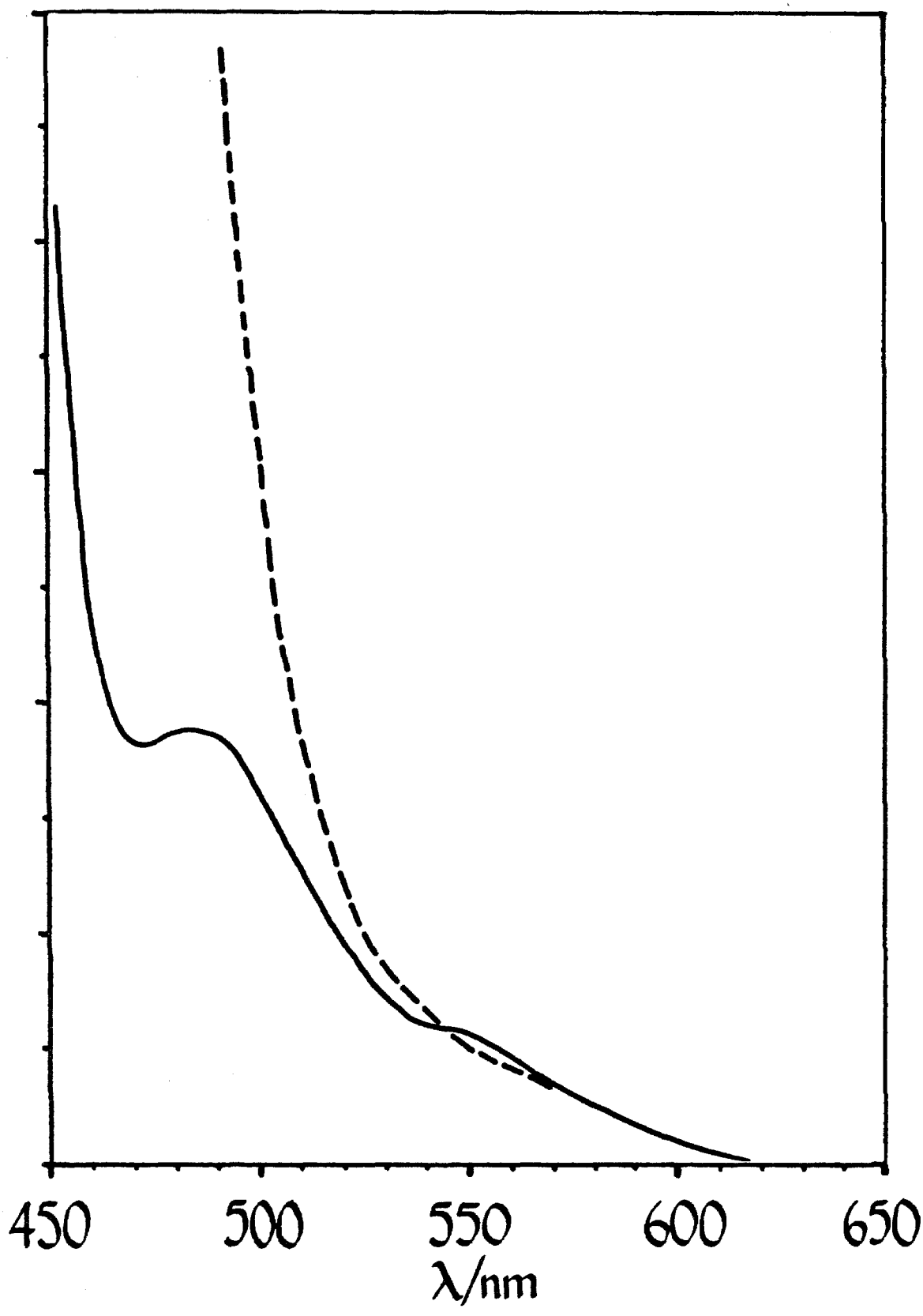
(a)



(b)



(c)



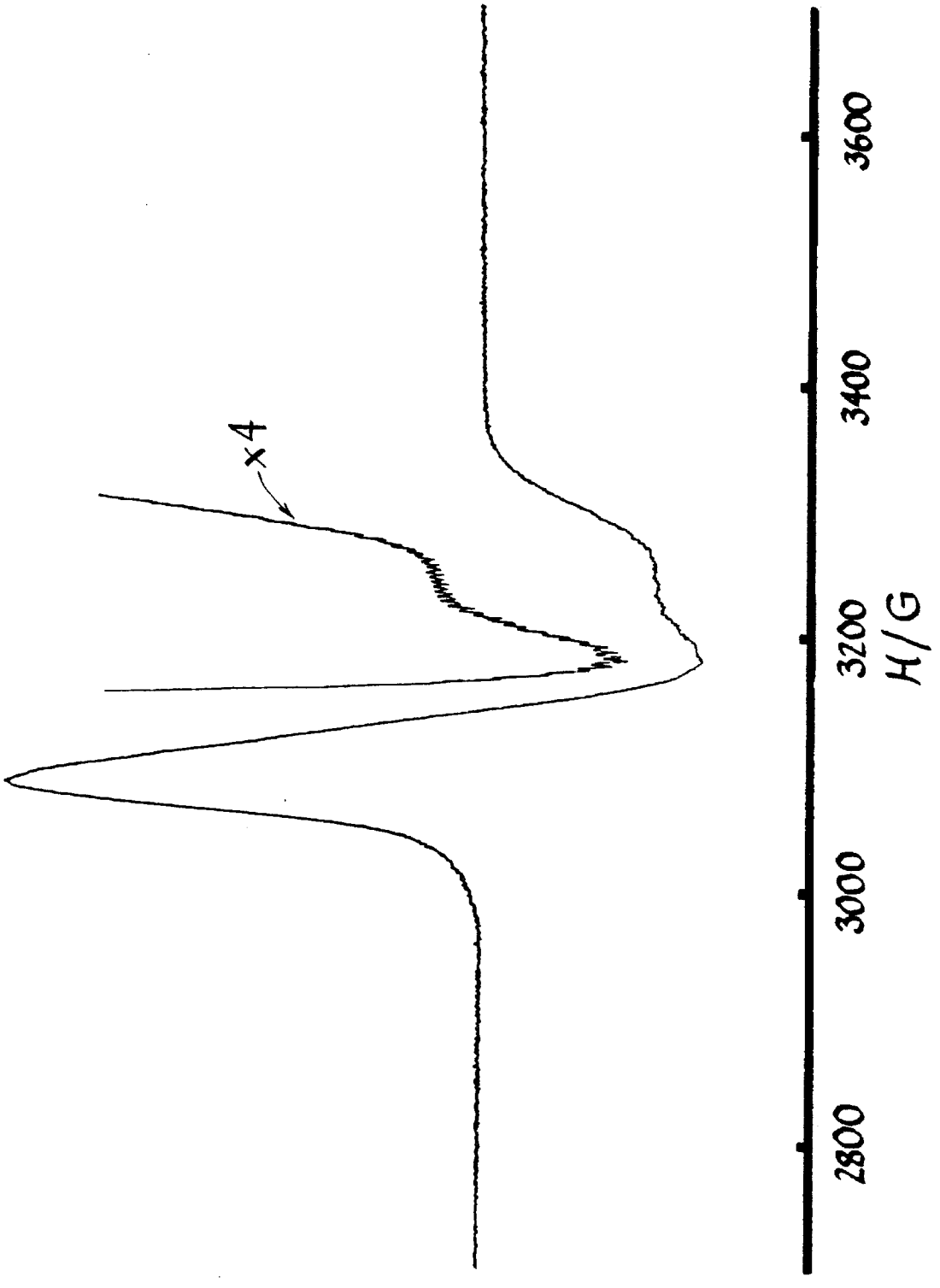
interpretation, luminescence is observed in solid $(Bu_4N)_2Mo_6Cl_{14}$ on excitation at 532 nm (Nd:YAG laser) even at ca. 30 K.

These data for weak absorption features are also roughly consistent with observed emission lifetimes, using the approximation of Strickler and Berg[43] for dipole-allowed transitions. For the weak shoulder at 590 nm in $(Bu_4N)_2Mo_6Cl_{14}$, the oscillator strength is approximately 6×10^{-7} and the expected radiative lifetime is ca. 8 ms. This compares favorably with an observed radiative lifetime of 4.1 ms for $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN (assuming unit quantum yield for formation of the luminescent excited state).

Herein are also reported the results of EPR measurements made on a frozen solution of electrochemically generated $Mo_6Cl_{14}^-$ (see section C of this chapter). The spectrum is presented in Figure 9. The signal can be accounted for by an axially symmetric S = 1/2 system, $g_\perp = 2.10$ and $g_\parallel = 2.0$. This signal decreases markedly in intensity as the temperature is raised and is detectable only with difficulty above 40 K. Powdered samples of $(Bu_4N)_2M_6X_{14}$ appear to give weak triplet EPR signals, but these are likely attributable to small quantities of O_2. I had hoped that it would be possible to observe the $Mo_6Cl_{14}^{2-*}$ excited state directly; but no change was observed in the EPR spectrum of $(Bu_4N)_2Mo_6Cl_{14}$ on irradiation.

Discussion. Theoretical studies and spectral assignments. Several general conclusions may be drawn from the optical spectra. The pronounced red shift in the absorption bands on changing from $Mo_6Cl_{14}^{2-}$ to $Mo_6Br_{14}^{2-}$ suggests an LMCT assignment for the intense bands in the near ultraviolet, and this is supported by studies at low temperature (vide

Figure 9. X-band EPR spectrum, recorded at ca. 10 K (9.23 GHz), for electrochemically generated $Mo_6Cl_{14}^-$ in frozen CH_2Cl_2.


x4
2800
3000
3200
3400
3600
H/G

supra). The two ions have very similar emission spectra, however; thus the transition observed in emission is likely to be localized on the Mo_6 core. Also, emission intensities are significantly greater for Mo than for W. This might be expected on grounds of spin-orbit coupling if the transition observed in emission were spin-forbidden.

The strong temperature dependence of the clusters' luminescence spectra (Fig. 6) is puzzling. Shifts in emission energy substantially greater than kT, such as are observed here, cannot be explained by vibrational components of a single electronic transition. A system with several thermally equilibrated excited states, having different emission spectra, could account for the temperature effects; but there is no evidence from band shapes or from lifetimes that the emission is composite. An additional possibility is that the electronic properties of the clusters are significantly altered by some type of phase change as the solid is cooled, but it appears that the question cannot be resolved with the current data.

After the substantial success of crystal and ligand field models in rationalizing the spectroscopic and magnetic properties of simple metal complexes, it was natural that systems of greater electronic complexity should be tackled. The octahedral halide clusters of Nb, Mo, Ta and W were a logical choice. First, not only was their high symmetry esthetically pleasing, but it also seemed ideal for typical symmetry-oriented theoretical studies. And second, the great chemical stability of the complexes in general, and the pronounced differences in properties between the group V and group VI clusters, were formidable problems for which sound theoretical insight might prove valuable.

Most of the theoretical treatments of the $M_6X_8^{4+}$ clusters are consistent with a simple bonding picture: the 24 d electrons in the central core just suffice to form a single bond along each edge of the octahedron. From such a model the strength and stability of the cluster unit follow nicely, and the ground state is neatly resolved in terms of its supposed diamagnetism. Kettle extended this principle to an appealing comparison with the larger group V clusters.[44] He suggested that 16 electrons from the face-bridging chlorides in $Mo_6Cl_8^{4+}$ be added to the 24 d electrons for bonding purposes. The $Ta_6Cl_{12}^{2+}$ ion is then complementary to $Mo_6Cl_8^{4+}$, with 16 d electrons from the Ta atoms and 24 from the twelve edge-bridging halides. This type of treatment, however, is consistent with only the most superficial analysis of the clusters' properties, and has little predictive power.

The first improvement over this qualitative approach was a group theoretical analysis by Duffey and co-workers.[45] The results of their treatment may be described with reference to the diagram of Figure 10. In this diagram the transformation properties of the molybdenum 4d, 5s and 5p and chlorine 3p orbitals are given (idealized symmetry O_h). Coordinate systems at the individual atoms are chosen so that all atomic z axes are radially directed. The orbitals are divided into five types of subset according to their transformation properties, and the designations used in Table 3 are used to label the resulting molecular orbital "bands" in Fig. 10. A few generalizations may be made from this energy diagram. The ϵ orbitals from Cl will be occupied and the σ and π from Mo (5p) empty. Although the Mo 4d and 5s will mix to some extent with the Mo 5p and Cl 3p, the strongest interactions should be among the 4d and 5s orbitals themselves. These interactions will then determine the

Figure 10. Qualitative molecular orbital diagram for $Mo_6Cl_8^{4+}$.

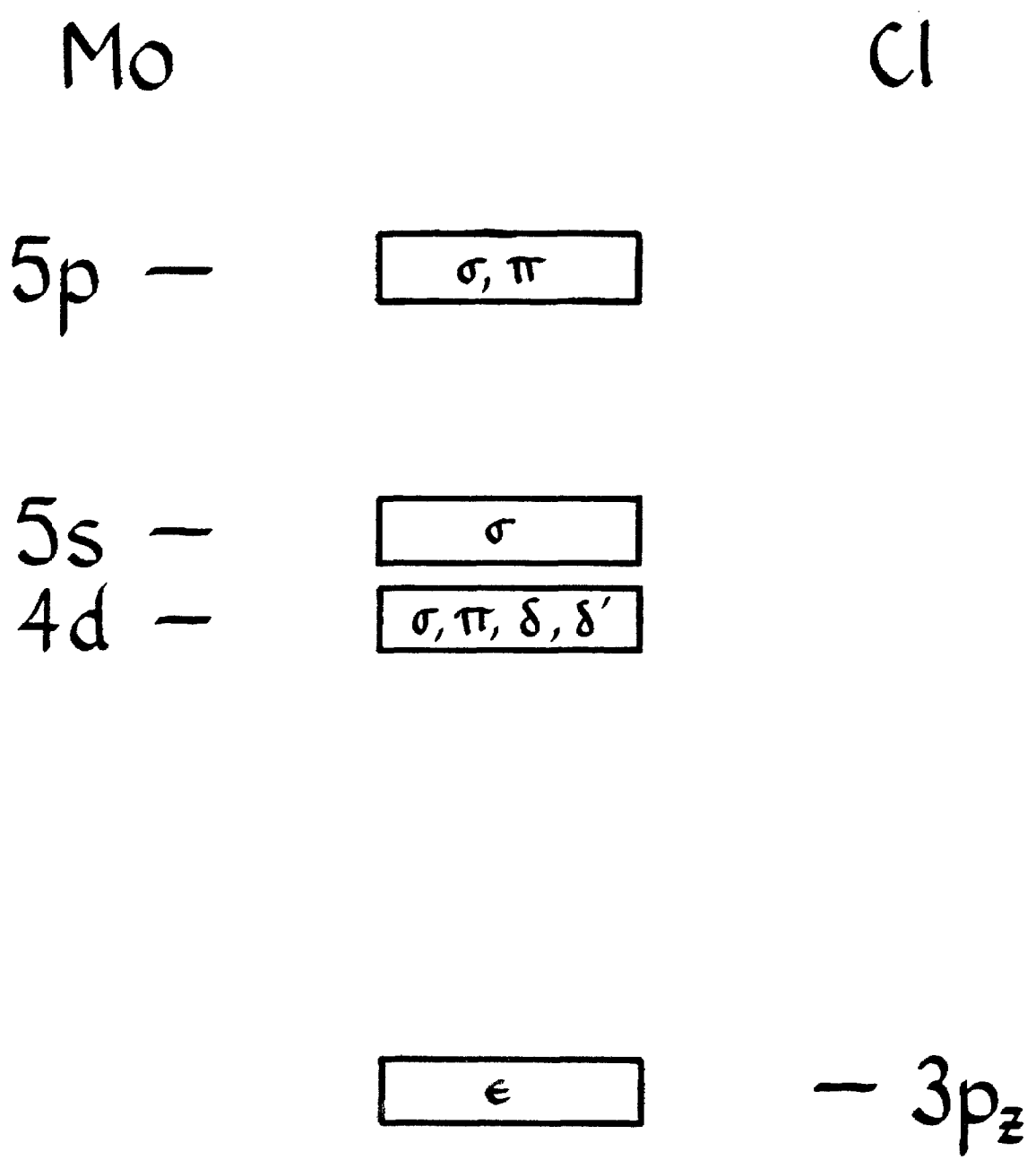

Mo
Cl
5p —
σ, π
5s —
σ
4d —
σ, π, δ, δ'
ϵ
— 3p_z

Table 3. Transformation properties for subsets of $Mo_6Cl_8^{4+}$ atomic orbitals.

	Constituent AOs	MOs	Designation
Mo	s, p_z, d_{z^2}	a_{1g}, e_g, t_{1u}	σ
	p_x, p_y; d_{xz}, d_{yz}	$t_{1g}, t_{1u}, t_{2g}, t_{2u}$	π
	d_{xy}	a_{2u}, e_u, t_{2g}	δ
	$d_{x^2-y^2}$	a_{2g}, e_g, t_{2u}	δ'
Cl	p_z	$a_{1g}, a_{2u}, t_{1u}, t_{2g}$	ϵ

ordering of the individual levels in which the remaining 24 electrons reside.

Several authors have attempted to provide energy level diagrams for these orbitals and thereby to give an accurate description of the cluster's electronic structure. Duffey and co-workers[45] gave the following five occupied levels: $a_{1g}(\sigma)$, $t_{2g}(\pi)$, $t_{1u}(\pi)$, $e_g(\delta')$ and $t_{2u}(\delta')$. Cotton and Haas,[46] in a study which also included an analysis of M_6X_{12} clusters, gave the same occupied levels for $Mo_6Cl_8^{4+}$. Their diagram included unoccupied levels as well, placing the $e_g(\sigma)$ level some 3 eV above the $t_{2u}(\delta')$ HOMO.

Guggenberger and Sleight added to their crystallographic study of $Mo_6Br_{12}.2H_2O$[47] an analysis of its electronic structure, considering first the idealized $Mo_6Br_8^{4+}$ (O_h) and then the changes on axial ligation of four Br^- and two H_2O. Although their results for the O_h core alone are very similar to those mentioned above, the HOMO-LUMO gap for the complete $Mo_6Br_{12}.2H_2O$ is more than twice as great (5.43 eV)! This gap is clearly inconsistent with their own observation of an orange color for the crystals as well as with the spectra reported herein and in ref. 21.

Two other theoretical studies, by Gibson and Meier[24] and by Briat and co-workers,[48] deal with essentially the same molecular orbitals but are designed to account for new experimental evidence; they will be discussed further below. Finally, a recent SCF-X_α-SW calculation on $Mo_6Cl_{14}^{2-}$ by Cotton and Stanley[49] gave the same five principally Mo-based orbitals. In addition, though, there were a number of other orbitals of predominantly Cl character interspersed among them, suggesting extensive interactions between Mo and Cl AOs. The HOMO-LUMO gap in

their study of some 2.1 eV agrees well with the ion's electronic spectrum, as does the profusion of predicted accessible excited states.

Another series of SCF-X_α-SW calculations deals with the $Mo_6X_8^{4+}$ ions (X = F, Cl, Br, I), comparing the MO energies as a function of X.[50] The orbitals were strongly localized on Mo or on X when X = F (a complex which has not been prepared!), and more heavily mixed for the other three halides. A related study compared observed and calculated photoelectron spectra.[51]

The semiempirical treatments of the M_6X_8 cluster electronic structure mentioned so far do not, unfortunately, accord well with several recent experimental results, notably magnetic data. Of these, the most readily accommodated were those of Gibson and Meier.[24] EPR spectra of γ-irradiated Mo_6Cl_{12} showed an isotropic signal at g = 1.943 and an axial signal with $g_\perp$ = 1.933 and $g_\parallel$ = 2.122. They ascribed the signals to $Mo_6Cl_8^{3+}$ and $Mo_6Cl_8^{5+}$ respectively. Their molecular orbital diagram includes the same levels as that of Cotton and Haas,[46] but with the ordering slightly different so as to make the LUMO $a_{2g}(\delta')$. With the HOMO still $t_{2u}(\delta')$, this leads to predicted ground states for $Mo_6Cl_8^{3+}$ and $Mo_6Cl_8^{5+}$ of $^2A_{2g}$ and $^2T_{2u}$, respectively, in qualitative agreement with their EPR data.

Another aspect of the clusters' magnetic properties that has recently come into question is their diamagnetism. Most authors have produced orbital schemes with closed-shell ($^1A_{1g}$) ground states and substantial HOMO-LUMO gaps. This is to be contrasted with the observation of Tjabbes, nearly fifty years ago, that Mo_6Br_{12} is probably weakly paramagnetic.[52] Additional data for other cluster derivatives[15,21,47,53] are generally in agreement with those of Tjabbes:

although the overall susceptibility is negative for each compound, standard diamagnetic corrections for the halide ions are always greater than the measured diamagnetism. Briat and co-workers extended the susceptibility measurements on Mo_6Cl_{12} to low temperature, finding χ_M = 3500 x 10^{-6} emu mol^{-1} at 4.2 K.[48] As additional evidence against a closed-shell ground state for the cluster they offer MCD spectra of $Mo_6Cl_8^{4+}$-containing poly(vinyl alcohol) films at 15 and 7.5 K, showing a number of signals whose intensity varies as T^{-1}. These MCD C terms exhibit maximum and minimum ellipticities at 380, 350, 310, 280 and 270 nm, in reasonable agreement with absorption maxima both in their own study and in Figure 4(a) here.

The C terms, along with the substantial magnetic moment, pointed to a paramagnetic ground state, or at least to a paramagnetic state as one of several thermally accessible states even at low temperature. I was interested in studying the temperature dependence of the cluster's magnetic susceptibility, as the measurements at room temperature[20] and 4.2 K[48] appeared to conflict. In Appendix I are described the results of such a study, performed on powdered $(Bu_4N)_2Mo_6Cl_{14}$. These show that the susceptibility remains negative even at 2 K. The slight temperature dependence of the susceptibility observed in this study may be ascribed to a small amount of some paramagnetic impurity. The diamagnetic susceptibility of ca. -630 x 10^{-6} emu mol^{-1} calculated for $(Bu_4N)_2Mo_6Cl_{14}$ is still smaller than that (ca. -760 x 10^{-6} emu mol^{-1}) estimated from Pascal constants for the nonmetal atoms. Perhaps this difference, as well as the discrepancies found at room temperature, is due to temperature-independent paramagnetism.

Thus the diamagnetism of the clusters at room temperature appears confirmed, in contrast to the observations of Briat and co-workers.[48] Further, their measurement of diamagnetism for $W_6Cl_8^{4+}$ [48] is in agreement with the results obtained here. The only point that remains to be resolved is the MCD C terms; these seem strongly indicative of an electronically degenerate ground state. Clearly more data are needed along these lines.

Finally, we come to an assessment of the theoretical studies of electronic structure for these clusters. It is apparent from the variety of energy level orderings in the various studies that the levels obtained and their energies are a sensitive function both of the basis sets used and of the calculation method. Even the assumption that those levels should be organized into "bands" as in Figure 9 is called into question by the results of the SCF-X_α-SW calculation of ref. 49, which indicated that the metal- and halide-based orbitals are not only mixed but closely intertwined.

It is possible that a detailed study of MCD spectra, previously conducted to great advantage in the assignment of the M_6X_{12} (M = Nb, Ta) cluster spectra,[54] might be useful for the $M_6X_{14}^{2-}$ and $M_6X_{14}^{-}$ ions as well. But the absorption features in the Nb and Ta clusters are conveniently arranged across a wide region of the optical spectrum. In the group VI species the absorptions are concentrated at high energy, where the individual bands can be run together or superimposed, and this makes the task considerably more difficult. One is tempted to conclude that, of the many electronic states possible for these clusters, even the lowest in energy cannot be predicted with current methods. Nevertheless, the experimental data reported here suggest strong similarities

among the three ions studied, and perhaps this would form a sound basis for a broad analysis of their electronic structure.

D. ELECTROCHEMISTRY

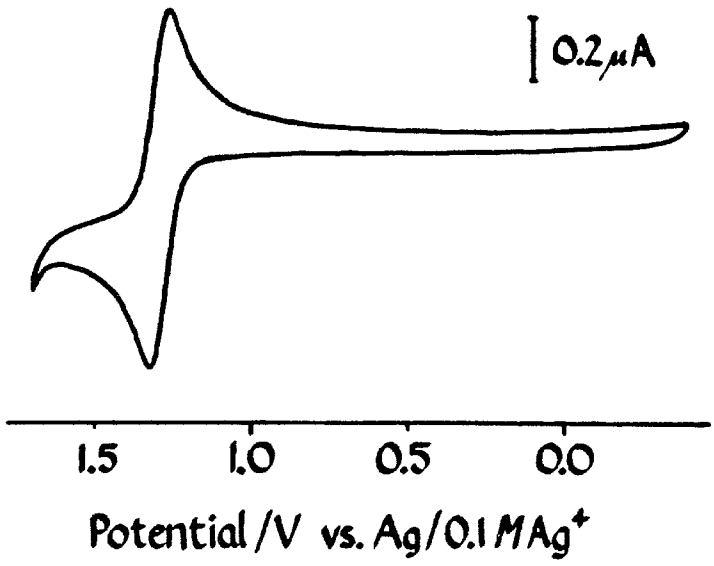
Redox reactions of the Mo and W clusters, as discussed in the Introduction to this chapter, have largely been confined to multielectron processes, frequently under relatively harsh conditions. Several factors led me to investigate the possibility of simpler electrochemical reactions in these compounds. One was the previous history of reversible redox behavior in other metal cluster systems: the M_6X_{12} halides of group V,[55] for example, and the tetrahedral organometallic cluster $[(\eta^5\text{-}C_5H_5)_4Fe_4(CO)_4]$.[56] Also, recent reports suggested[57] that many compounds whose redox reactions had been little studied might have rich electrochemistry. And finally, of the commonly known cluster complexes, the halides of group VI seemed most likely, for spectroscopic reasons, to possess excited states suitable for photochemical redox reactions.

As the previous studies of these clusters suggested that they were unaffected by mild oxidants and reductants, it appeared unlikely that aqueous solutions would be appropriate for electrochemical investigation. In acetonitrile, however, the $M_6X_{14}^{2-}$ ions display several features. Preliminary experiments with $Mo_6Cl_{14}^{2-}$ revealed an anodic wave at a potential approx. 0.5 V more positive than that required to oxidize Cl^- under the same conditions. Cathodic waves were also present, but these were more complicated and not easily resolved.

More detailed studies used Bu_4NTFMS as supporting electrolyte (0.1 M) and a silver - 0.1 M $AgNO_3$ (CH_3CN) reference electrode. The best data were obtained with working and counter electrodes of platinum. These showed nearly reversible, diffusion-controlled one electron oxidation waves. Figure 11 illustrates a typical cyclic voltammogram for

Figure 11. (a) Cyclic voltammogram for $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN. (b) Polarographic half-wave potentials $E_{1/2}$ for the three cluster ions in CH_3CN.

(a)



(b)

Ion	$E_{1/2}$ / V vs. Ag/Ag^+	vs. SCE (est.)
$Mo_6Cl_{14}^{2-}$	1.29	1.60
$Mo_6Br_{14}^{2-}$	1.07	1.38
$W_6Cl_{14}^{2-}$	0.83	1.14

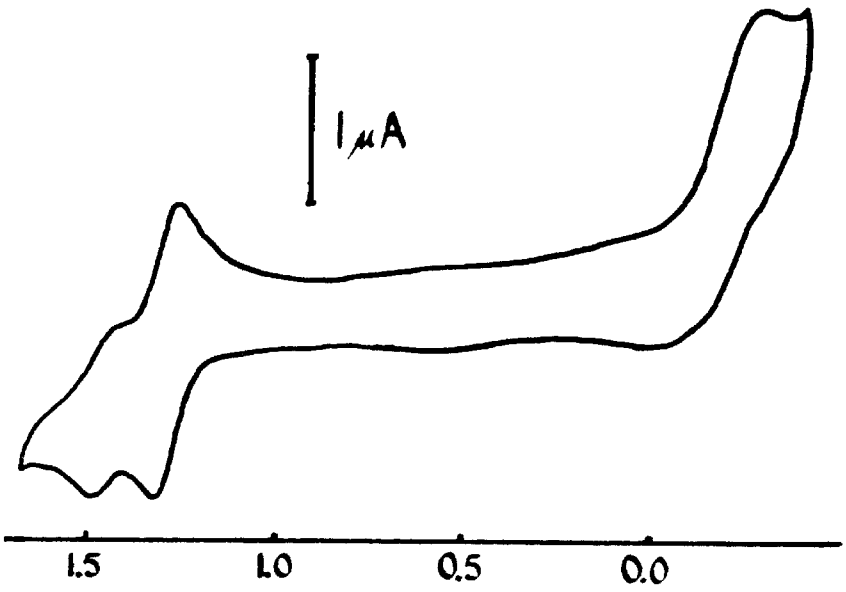
$Mo_6Cl_{14}^{2-}$ in CH_3CN, and gives half-wave potentials extracted from cyclic voltammograms for the three cluster ions.

In these cyclic voltammetry experiments plots of peak anodic current vs. (scan rate)$^{1/2}$ were linear over the following ranges: $Mo_6Cl_{14}^{2-}$, 20 mV s^{-1} to 500 V s^{-1}; $Mo_6Br_{14}^{2-}$, 20 mV s^{-1} to 1 V s^{-1}; $W_6Cl_{14}^{2-}$, 50 to 350 mV s^{-1}. Thus the redox reactions are not limited by electrode kinetics within these limits. In addition, the ratio of cathodic and anodic peak currents, calculated using Nicholson's approximation,[58] approaches unity at high scan rates for all three ions. At lower scan rates, however, the ratio drops significantly. Thus, although nearly all of the $M_6X_{14}^{-}$ produced anodically can be re-reduced at high scan rates, the ion is unstable over longer periods of time.

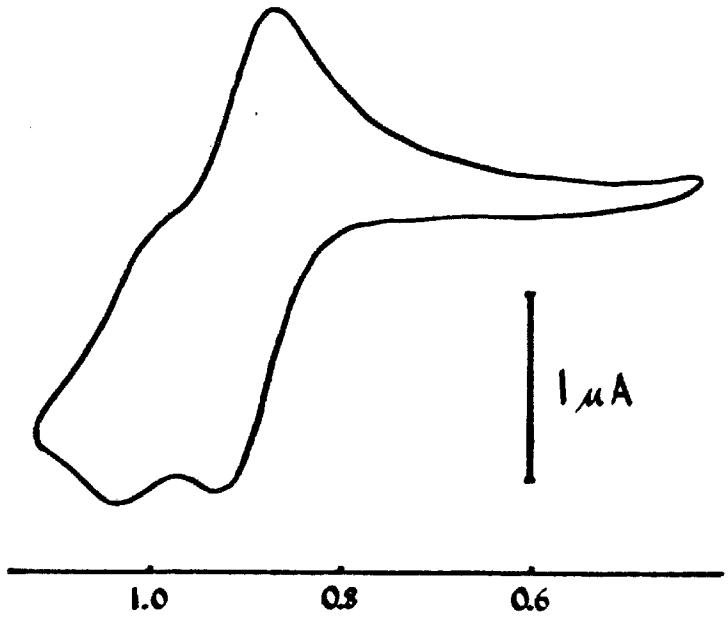
Bulk electrolysis experiments were also performed in an attempt to prepare the oxidized $M_6X_{14}^{-}$ species in pure form. In agreement with the results, mentioned above, of cyclic voltammetry experiments in acetonitrile, the attempt to prepare $Mo_6Cl_{14}^{-}$ in CH_3CN failed. Even after the passage of three equivalents of electrons through the solution, the resting potential of the cell, 1.26 V, indicated that oxidation was incomplete. Cyclic voltammograms recorded at this point showed a number of new waves (Figure 12(a)), indicating extensive chemical changes in the cluster. In dichloromethane, however, quantitative oxidations could be carried out for both $Mo_6Cl_{14}^{2-}$ and $W_6Cl_{14}^{2-}$. In both cases cyclic voltammograms were unchanged during electrolysis.

Absorption spectra of the electrolyzed CH_2Cl_2 solutions are presented in Figure 13. The $Mo_6Br_{14}^{2-}$ oxidation proceeded quantitatively as well. But in this case the oxidation product gives a cyclic voltammogram (Figure 12 (b)) different from that of the starting

Figure 12. Cyclic voltammograms obtained after attempted bulk electrolyses. (a) $Mo_6Cl_{14}^{2-}$ in CH_3CN. (b) $Mo_6Br_{14}^{2-}$ in CH_2Cl_2.

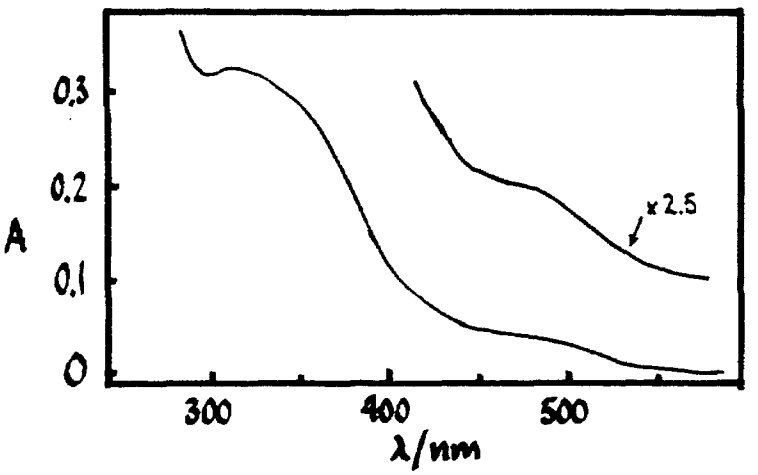


(a)

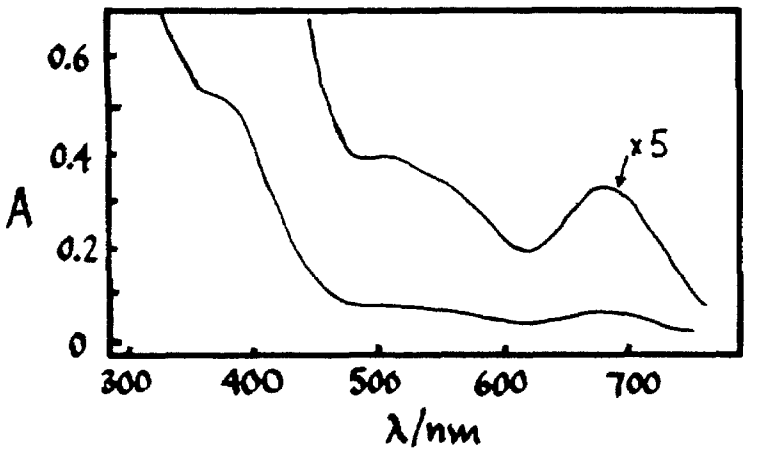


(b)

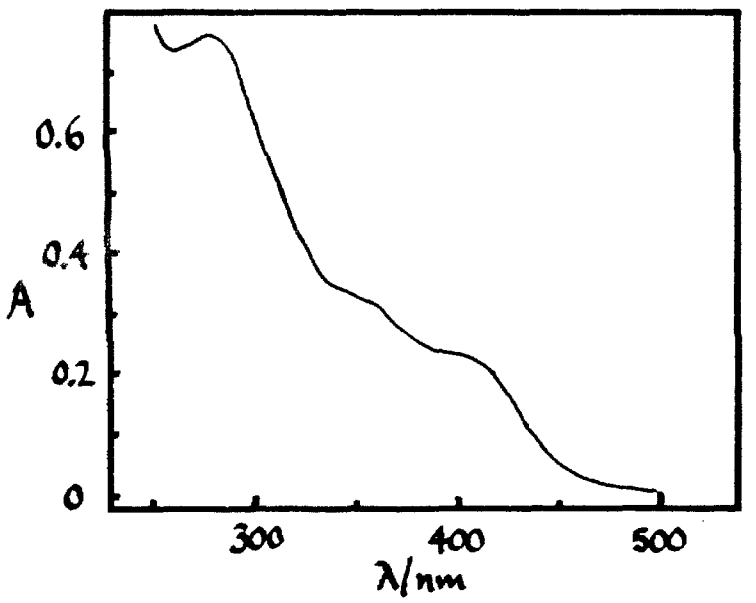
Figure 13. Absorption spectra (1 mm cell) of solutions obtained by bulk electrolysis in CH_2Cl_2. Solutions originally 1 mM in $M_6X_{14}^{2-}$. (a) $Mo_6Cl_{14}^{2-}$; (b) $Mo_6Br_{14}^{2-}$; (c) $W_6Cl_{14}^{2-}$.


0.3
0.2
0.1
0
A
x 2.5
300
400
500
λ/nm

(a)


0.6
0.4
0.2
0
A
x 5
300
400
500
600
700
λ/nm

(b)


0.6
0.4
0.2
0
A
300
400
500
λ/nm

(c)

material. Here a comparison of the bulk electrolysis results is of interest. $Mo_6Cl_{14}^{2-}$ gives secondary reactions on oxidation in CH_3CN; both it and $W_6Cl_{14}^{2-}$ can be oxidized reversibly in CH_2Cl_2; and $Mo_6Br_{14}^{2-}$ undergoes further reaction upon oxidation even in CH_2Cl_2. This suggests that the decompositions may involve solvent molecules (or fragments thereof) reacting with $M_6X_{14}^{-}$. For $Mo_6Cl_{14}^{2-}$, the previous report of DMSO- and DMF-substituted complexes[19] makes the formation of species such as $Mo_6Cl_{13}(CH_3CN)^{-}$ plausible. And in CH_2Cl_2, where solvent and substrate have a common anionic component, both the $M_6Cl_{14}^{-}$ ions should be relatively stable. With $Mo_6Br_{14}^{2-}$, the possibility of ligand exchange remains even in dichloromethane.

An additional point of interest with respect to the possibility of multielectron transfer reactions (see section F; compare refs. 26 and 27) is the existence of an additional anodic wave for $W_6Cl_{14}^{2-}$. This wave is not as simple as the first one, and may itself involve the transfer of more than one electron. $W_6Cl_{14}^{2-}$ is the only one of the three ions examined whose first oxidation takes place well before solvent decomposition. Thus it is not surprising that additional oxidation should be evident here and not in the other two ions.

Thus all three cluster ions undergo simple one electron oxidation in aprotic solvents. The products are powerful oxidizing agents, rivaled by only a few chemical oxidants. Also, the position of the oxidation waves relative to those of the free halide ions confirms that the halides in $M_6X_{14}^{2-}$ are firmly bound. Side reactions of the oxidized species, probably including ligand exchange with solvent, interfere with large-scale electrochemical preparations in some cases. The side reactions can, however, be minimized by choice of solvent; and in any case,

for the purposes of rapid reactions, the powerful oxidants $M_6X_{14}^-$ are essentially stable.

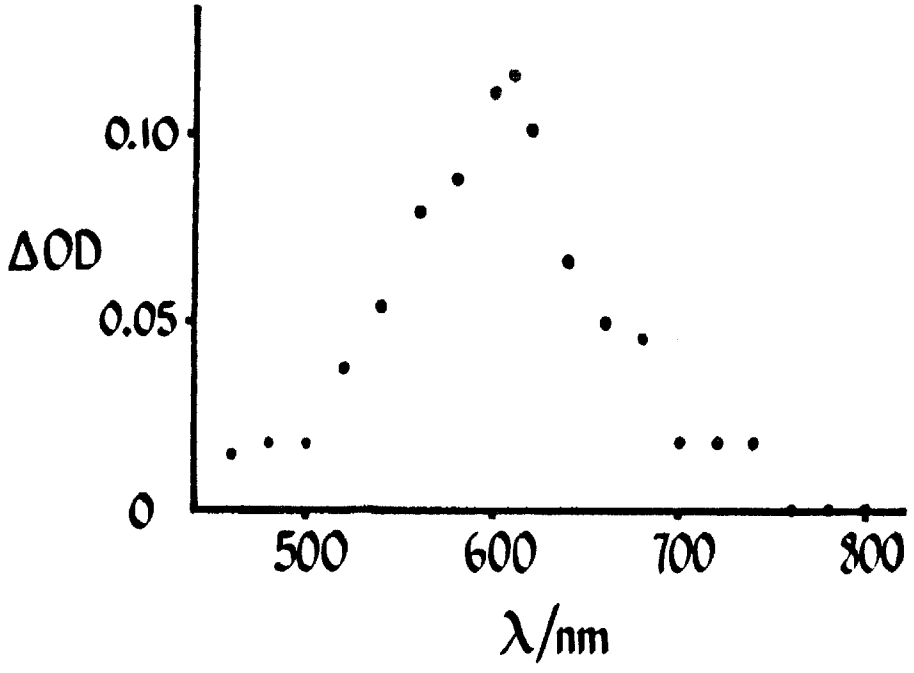
E. PHOTOCHEMISTRY

The cluster ions described here share several features that make them attractive for photochemical studies. The first is the chemical stability of the cluster unit under a variety of conditions, extensively documented in the literature. Second, they undergo simple one-electron redox reactions, again without major structural change. Third, the ions absorb strongly in the visible and near-ultraviolet regions. And finally, the luminescence of the clusters, unusually long-lived especially in the case of $Mo_6Cl_{14}^{2-}$, suggests that they might be able to participate effectively in photochemical reactions. This section deals with the photoredox chemistry of $Mo_6Cl_{14}^{2-}$ in aqueous and nonaqueous solution.

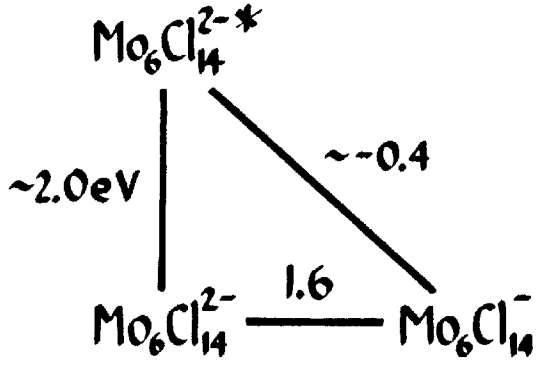
The combination of attractive photophysical and electrochemical properties in $Mo_6Cl_{14}^{2-}$ led me to investigate the effects of added electron acceptors. Methylviologen (MV^{2+}) has been used extensively as an electron transfer quencher because of its radical cation's properties as a powerful and relatively stable reductant (E^o = -0.446 V vs. NHE[31]) and as an intensely colored species that can be identified readily in flash kinetic spectroscopic studies. Figure 14(a) illustrates the data obtained from such an experiment with MV^{2+} and $Mo_6Cl_{14}^{2-}$ in acetonitrile. The transient difference spectrum shown agrees closely with that of MV^{+}.[32] Separate experiments show that the emission of $Mo_6Cl_{14}^{2-}$ is efficiently quenched by MV^{2+}; and these results together indicate that the quenching proceeds by electron transfer from $Mo_6Cl_{14}^{2-*}$.

The quenching of $Mo_6Cl_{14}^{2-*}$ is illustrated by reaction (2), written for a general electron acceptor A:

Figure 14. (a) Transient difference spectrum recorded 80 μs after flash irradiation ($\lambda > 380$ nm) of a solution of MV^{2+} and $Mo_6Cl_{14}^{2-}$ in CH_3CN. (b) Modified Latimer diagram for $Mo_6Cl_{14}^{2-}$ in CH_3CN (estimated electrode potentials/V vs. SCE).


0.10
ΔOD
0.05
0
500
600
700
800
λ/nm

(a)


$Mo_6Cl_{14}^{2-*}$
~2.0eV
~-0.4
1.6
$Mo_6Cl_{14}^{2-}$
$Mo_6Cl_{14}^{-}$

(b)

$$Mo_6Cl_{14}^{2-*} + A = Mo_6Cl_{14}^{-} + A^{-} \quad (2)$$

$$Mo_6Cl_{14}^{-} + A^{-} = Mo_6Cl_{14}^{2-} + A \quad (3)$$

In reaction (3) the transferred electron is returned to its original position.

Further use of MV^{2+} in this system was complicated by a solubility problem: it forms a precipitate with $Mo_6Cl_{14}^{2-}$ which is nearly insoluble in aqueous HCl and only sparingly soluble in CH_3CN.

Other experiments were performed using neutral and anionic quenchers to circumvent this problem. Possible oxidative quenchers for nonaqueous solutions were selected from the compilation of Mann and Barnes.[59] In flash kinetic spectroscopic experiments with TCNE (in CH_2Cl_2) or chloranil (in CH_3CN) along with $Mo_6Cl_{14}^{2-}$, transient difference spectra showed signals attributable to the quenchers' radical anions.[60-62] The criterion used to determine reversible electron transfer chemistry in these experiments was the successful fitting of data for the back electron transfer reaction (3) to the expected second order kinetics. The transient absorptions in these two cases indeed decayed with second order kinetics, with rate constants k_3 of ca. 3.0×10^9 and 1.1×10^8 M^{-1} s^{-1} respectively.

In order to establish that the redox properties of $Mo_6Cl_{14}^{2-}$ also apply to aqueous solutions I examined two types of water-soluble quenchers. The luminescence of $Mo_6Cl_{14}^{2-}$ is easily detectable in hydrochloric acid solution (Table 2); but other solutions are unsatisfactory: at higher pH hydrolysis reactions result in the formation of precipitates,[20] and in other acidic media, such as dilute H_2SO_4, the complex appears no longer to luminesce. Accordingly, flash kinetic

spectroscopic experiments in aqueous solution were restricted to 2-3 M HCl. It appeared that, if the use of MV^{2+} as quencher was hampered by solubility problems, sulfonation might solve that problem by making the viologen a zwitterion. In fact, the best results were obtained with the sulfoalkylated bipyridines BSEP and BSPP. For example, the rate constant k_3 for $BSEP^-$ was 1.0×10^9 M^{-1} s^{-1} (the kinetics of reaction (3) in this case were satisfactory over a range of at least a factor of four in $[BSEP^-]$).

As a set of quenchers for aqueous solutions the Keggin $XW_{12}O_{40}$ heteropolytungstates appeared ideal for several reasons. First, especially in the presence of heterogeneous catalysts, the viologens are subject to hydrogenation,[30] which wastes stored energy and destroys their electron relay properties. Second, the heteropoly ions undergo clean electron transfer reactions in acidic aqueous solutions. Here the choice of central atom X (for example, among the series $PW_{12}O_{40}^{3-/4-}$, $SiW_{12}O_{40}^{4-/5-}$, and $BW_{12}O_{40}^{5-/6-}$) in the Keggin ions allows variation both in charge and in redox potential (-0.07, -0.27 and -0.58 V vs. SCE respectively).[34] Thus, under the conditions (2-3 M HCl) employed in these studies, both $SiW_{12}O_{40}^{5-}$ and $BW_{12}O_{40}^{6-}$ are thermodynamically capable of reducing H^+ to H_2. And finally, the fully oxidized W(VI) species are colorless, while the one electron reduced "heteropoly blues" show broad absorption in the red and near-infrared regions.[63] Unfortunately, although the heteropoly ions appear to quench the $Mo_6Cl_{14}^{2-}$ luminescence efficiently (see below), repeated trials in flash kinetic spectroscopic experiments failed to confirm second order behavior for reaction (3). Perhaps some impurity interferes with the back electron transfer

reaction as written, making the kinetics for disappearance of the heteropoly blue ion pseudo-first order.

The classical Stern-Volmer analysis, which treats competing uni- (luminescence and nonradiative decay) and bimolecular (quenching) reactions, was used in an examination of the kinetics of reaction (2). For TCNE in CH_3CN, where the driving force for reaction (2) is approx. 0.6 V,[59] the value for k_2 was 2.5 x 10^9 M^{-1} s^{-1}, near the diffusion limit as expected. With BSEP in 2 M HCl, where the driving force is much smaller (both BSEP and BSPP show reversible waves at potentials close to that of MV^{2+}), the measured rate constant was 3.8 x 10^6 M^{-1} s^{-1}. Preliminary data, also in 2 M HCl, for BSPP, $PW_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$ suggest values of k_2 of approx. 3 x 10^6, 7 x 10^8 and 2 x 10^8 M^{-1} s^{-1} respectively (although the full analysis of electron transfer kinetics has not been successful in either case; see above).

Thus the luminescent excited state of $Mo_6Cl_{14}^{2-}$ is capable of rapid reaction with electron acceptors, producing the powerfully oxidizing $Mo_6Cl_{14}^{-}$. The data for BSEP in particular confirm that the ion's attractive photochemical properties, originally inferred from its photophysical and electrochemical behavior in nonaqueous media, are retained in aqueous solution as well. These properties, namely the presence of long-lived excited states and the capacity for rapid thermal and photochemical redox reactions without major structural change, are expected to persist in the $Mo_6Br_{14}^{2-}$ and $W_6Cl_{14}^{2-}$ ions also.

F. PROSPECTS

The significance of the results reported herein can be evaluated on several fronts. With respect to the fundamental understanding of electronic structure, the situation is somewhat disappointing. Even in a system as electronically complex as this one, it would be encouraging if a number of theoretical studies, based on different assumptions, were in substantial agreement. However, the calculations performed to date have given partially conflicting results. It is difficult to decide which of these studies reproduces the experimental data most accurately. Perhaps a detailed multielectron calculation would provide a better rationalization of the experimental results. But one could not be highly confident of such an improvement in advance. It seems unlikely, then, that current theoretical methods will be of great assistance in explaining the electronic structure of the M_6X_8 cluster species. Even the analysis (mentioned in section C) of the Nb and Ta halide clusters,[53] although successful in explaining spectral properties, offers little chemical insight. Thus those who look for a theoretical rationale for the thermal and photochemical reactions of these clusters may be disappointed.

The outlook is considerably brighter on the experimental side. These results represent the beginnings of a detailed study of spectral and magnetic properties, redox reactions and photochemistry for a series of compounds that has previously received little such attention. Based on the data discussed here, the cluster complexes are expected to share many properties; and thus the variety of specific M_6X_8 clusters already in the literature makes the prospect of subtle variations in these characteristics very good. One promising route to minor spectral and

redox changes is the partially formed cluster ion $Mo_5Cl_{13}^{2-}$, apparently produced as an intermediate in the reduction of $MoCl_6^{3-}$ by Bi,[16] and through which clusters with one heteroatom (e.g. Nb or W) might be accessible. A greater change in properties might be expected for the cationic $[M_6X_8]L_6^{4+}$ complexes,[19] and these should certainly be examined.

Also worthy of exploration are the variety of photoredox reactions possible even in the simple $M_6X_{14}^{2-}$ series. The kinds of photoredox reactions expected are two, one documented here and the other as yet little explored.

The first type of reaction, discussed in Section E of this chapter, begins with one electron transfer reaction of the cluster excited state. These properties are not unique to the $M_6X_{14}^{2-}$ clusters; they have been exploited in a number of sensitizers. In particular, bimolecular electron transfer reactions of excited states, as photochemical sources for powerful oxidants and reductants, have found wide use in schemes for energy storage.[6] Two specific properties of these clusters suggest that their use in such systems may be advantageous. The first is their composition: although the other sensitizers in common use rely on organic ligands as contributors to their photochemically attractive excited states, these clusters possess similar properties despite being constructed only of metal and halogen atoms. And second, their redox potentials lie within a useful range: the photogenerated oxidant $Mo_6Cl_{14}^{-}$, for example, is thermodynamically powerful enough to oxidize water or chloride ion even in strongly acidic solution. One direction in which research with these clusters might continue, then, would be further explorations of their potential for energy storage based on one-electron schemes. The goal here would be to couple reactions (2)

and (3), which generate $Mo_6Cl_{14}^-$ and A^-, with additional reactions to complete a redox cycle, for example,

$$A^- + H^+ = A + 1/2\ H_2 \qquad (4)$$

$$Mo_6Cl_{14}^- + 1/2\ H_2O = Mo_6Cl_{14}^{2-} + H^+ + 1/4\ O_2 \qquad (5)$$

Although the various problems associated with the promotion of these H_2- and O_2-producing reactions now receive a great deal of attention, it is possible that the clusters, as durable all-inorganic species made from relatively inexpensive metals, can make a valuable contribution in this area.

The second possibility, the more ambitious of the two, would be the exploration of the clusters' capacity for direct multielectron transfer. Reactions (4) and (5) above would probably require heterogeneous catalysts in order to proceed at reasonable rates. But another approach would be to take advantage of the strongly acidic solutions used with $Mo_6Cl_{14}^{2-}$, in which the cluster ion may engage in protonation equilibria:

$$Mo_6Cl_{14}^{2-} + H^+ = HMo_6Cl_{14}^- \qquad (6)$$

$$HMo_6Cl_{14}^- + H^+ = H_2Mo_6Cl_{14} \qquad (7)$$

The protonated forms will probably have similar types of excited states, which could undergo bimolecular (8) or unimolecular (9) two electron oxidation:

$$HMo_6Cl_{14}^{-*} + H^+ = Mo_6Cl_{14} + H_2 \qquad (8)$$

$$H_2Mo_6Cl_{14}^* = Mo_6Cl_{14} + H_2 \qquad (9)$$

Judging from the one electron potentials measured here, the two-electron oxidized Mo_6Cl_{14} produced in this scheme would be a very powerful oxidant, probably readily capable of oxidizing water or Cl^-. However, this same logic suggests that the excited state might not have enough energy to drive the two-electron reaction as written. The clusters for which this type of reaction is most likely, then, are those with the lowest electrode potentials for oxidation; clearly $Mo_6Cl_{14}^{2-}$ is at a disadvantage. Except for its lower emission quantum yield, $W_6Cl_{14}^{2-}$ would be best of all because it is relatively easy to oxidize. In addition, it is the only one of the three ions studied here that gives definite elctrochemical evidence for more highly oxidized species. The previous redox studies of the $W_6Br_8^{4+}$ - $W_6Br_8^{6+}$ system,[26,27] with its overall two-electron transfer, offer encouragement for the scheme of reactions (8) and (9).

Thus the studies reported herein, which expand the experimental treatment of photophysics and spectroscopy for these clusters and provide an early account of their photoredox reactions, open a number of areas for further research. Progress is also anticipated for the studies of electronic structure, although these efforts may be hampered in the short term by the absence of a detailed theoretical framework. But the clusters represent a new type of photochemical system, and it is likely that a number of features of these systems will be of use in photoredox reactions.

CHAPTER III

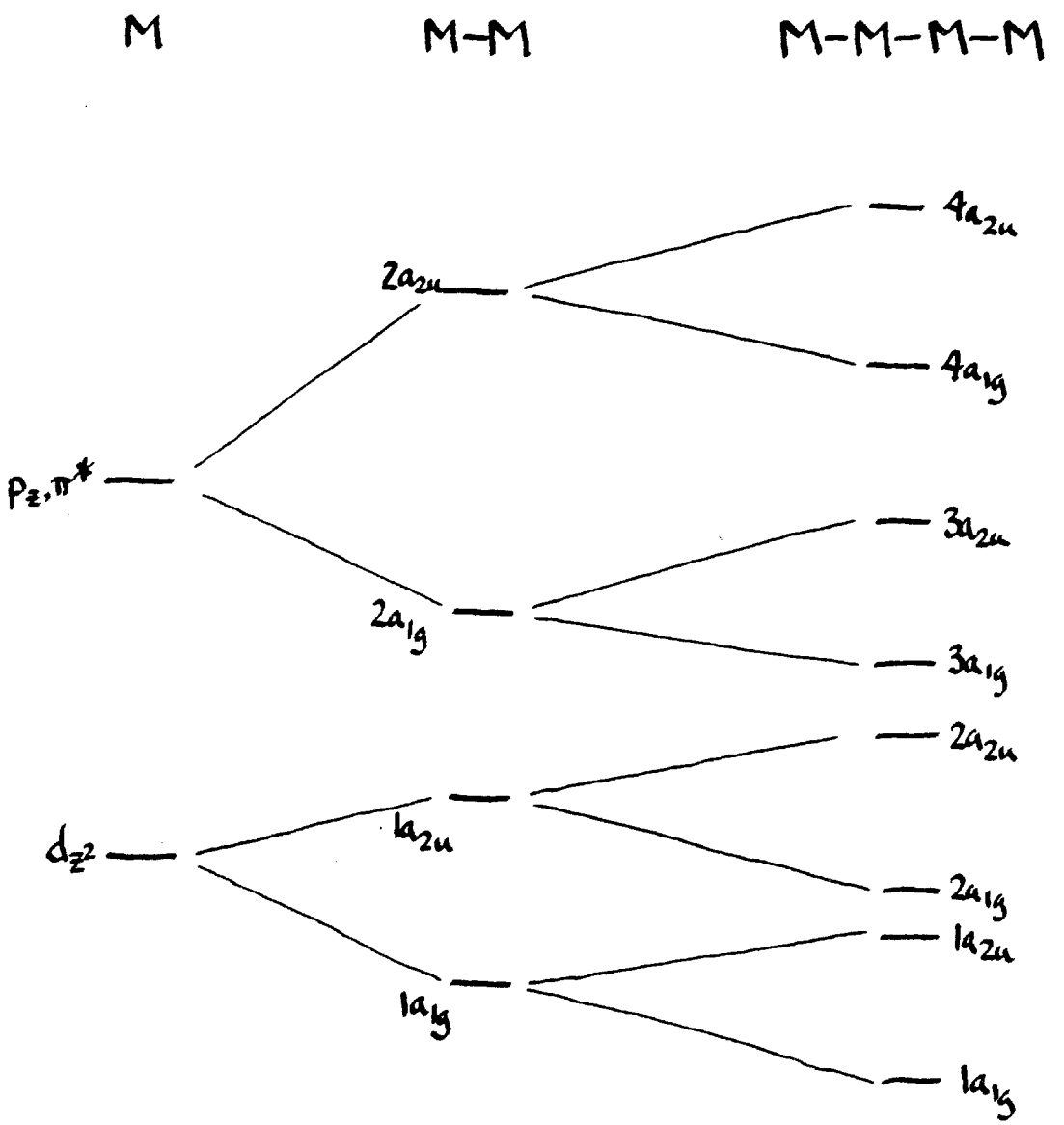
RHODIUM ISOCYANIDE COMPLEXES

A. INTRODUCTION

Studies of the photophysical and photochemical properties of planar d^8 complexes date from the experiments of Geoffroy and co-workers,[64] who examined the electronic absorption and emission spectra of several rhodium(I) and iridium(I) phosphine complexes. In these mononuclear complexes the principal low-energy absorption and emission features are qualitatively explained in terms of the molecular orbital diagram in Figure 15(a). In idealized symmetry D_{4h} the d^8 ground state is $^1A_{1g}$ ($(d_{z^2})^2$), and the emissive excited state is the lowest triplet, $^3A_{2u}$ ($(d_{z^2})^1(p_z, \pi^*)^1$). Subsequent studies in this laboratory have concentrated on the properties of rhodium(I) isocyanide complexes. The most striking observation here was their oligomerization in solution:[65,66] for a variety of isocyanides CNR the complexes $Rh(CNR)_4^+$ were shown to exist in equilibrium with strongly colored species $Rh_n(CNR)_{4n}^{n+}$ (n = 2, 3, 4). Finally several such complexes were prepared with diisocyanoalkane ligands in order to isolate a specifically binuclear ion; the first such ion, $Rh_2b_4^{2+}$ ("b", or "bridge", = 1,3-diisocyanopropane)[67,68] has since received the greatest amount of attention.

The spectroscopic properties of $Rh_2b_4^{2+}$ and related complexes of other diisocyanides have been extensively studied. The redox reactions and photophysics of the $Rh_2b_4^{2+}$ ion may again be qualitatively associated with the diagram in Figure 15. In the Rh(I) oxidation state the $1a_{1g}$ and $1a_{2u}$ levels are filled, and the metal-metal interaction, though formally nonbonding, is slightly attractive as a result of configuration interaction with the unoccupied $2a_{1g}$ and $2a_{2u}$ levels. Oxidation to Rh(II) ($(1a_{1g})^2$) results in the formation of a full single Rh-Rh bond.

Figure 15. Qualitative metal–metal σ and π^* interactions in mono-, di- and tetranuclear square complexes (D_{4h}).


M
M-M
M-M-M-M
$4a_{2u}$
$2a_{2u}$
$4a_{1g}$
p_z, π^*
$3a_{2u}$
$2a_{1g}$
$3a_{1g}$
$2a_{2u}$
d_{z^2}
$1a_{2u}$
$2a_{1g}$
$1a_{2u}$
$1a_{1g}$
$1a_{1g}$

The Rh(II) species, yellow in color due to the relatively high energy required for the $\sigma \rightarrow \sigma^*$ transition, are conveniently prepared by oxidative addition to $Rh_2b_4^{2+}$. The intermediate oxidation state $Rh_2b_4^{3+}$ is a radical but can be stabilized by dimerization to $Rh_4b_8^{6+}$, $(1a_{1g})^2(1a_{2u})^2(2a_{1g})^2$. Spectroscopically, all complexes should display strong absorption bands, those at lowest energy being essentially $\sigma \rightarrow \sigma^*$ for $Rh_2b_4^{4+}$ and $Rh_4b_8^{6+}$, and $\sigma^* \rightarrow \sigma$ for $Rh_2b_4^{2+}$. In $Rh_2b_4^{2+}$ the lowest excited configuration gives rise to $^1A_{2u}$ and $^3A_{2u}$ terms, both of which can undergo luminescence. Fluorescence was observed early on in these binuclear complexes,[68] in contrast to the mononuclear species, which appear only to phosphoresce. At that time a relatively long-lived (ca. 8 μs) transient absorption signal was attributed to the triplet state, but its phosphorescence was not recorded until several years later.[40] This study of the $^3A_{2u}$ state recorded both its emission properties and its one electron oxidation and reduction reactions. Thus $Rh_2b_4^{2+}$, like $Ru(bpy)_3^{2+}$ [8] and $Mo_6Cl_{14}^{2-}$ (Chapter II.), possesses a long-lived excited state which acts as a good redox agent.

The study of these bimolecular excited-state reactions, then, is a relatively recent area of inquiry for the rhodium isocyanide complexes, and one that makes them spectroscopically similar to other commonly used transition metal sensitizers. But the original photochemical interest in these complexes came from a different type of reaction. Shortly after the initial accounts of the spectra and simple reactions of $Rh_2b_4^{2+}$ in nonaqueous solution, the ion was shown[68] to form deep blue solutions in hydrohalic acids. These solutions were photosensitive, giving H_2 and $Rh_2b_4^{4+}$ in degassed concentrated HX (X = Cl, Br). That $Rh_2b_4^{4+}$ reacts spontaneously with hydrogen in HX solution, giving the

blue solutions again, seemed a reliable indication that the photochemical evolution of H_2 was an energy-storing process.

The identification of the blue species formed from $Rh_2b_4^{2+}$ in aqueous acidic solution was a long process. At first a hydride, perhaps the oxidative addition product $HRh_2b_4^{3+}$, was proposed. Such a structure might explain its ability to produce hydrogen photochemically. But no evidence was found in NMR or IR spectra, or in isotope studies of reaction rates, for a metal hydride. Meanwhile flash kinetic spectroscopic experiments were carried out on solutions made from $Rh_2b_4^{2+}$ in H_2SO_4, where hydrogen is not produced photochemically. Irradiation of the intense absorption band at 558 nm in these solutions produced a transient signal that decayed with second-order kinetics.[69,70] In addition, an analysis of the ionic strength dependence of the back reaction rate constant suggested that the reacting species were both 3+ ions. Thus the photosensitive species was not a simple binuclear complex; a tetranuclear species was more likely. Although there was some evidence that intensely colored oligomeric species could form at high $Rh_2b_4^{2+}$ concentrations,[67] their spectra did not match well with that observed, and in any case the H_2SO_4 solutions appeared to contain a single species and not an equilibrium mixture.

Several other experiments were crucial in establishing that the "blue" solutions contained tetranuclear species involving partial oxidation of Rh. First, a reinvestigation[71] of the hydrogen-producing reaction in conc. HCl showed that equal quantities of H_2 were released in two steps, the first thermal and the second photochemical. Redox titrations with Ce(IV) and Cr(II) solutions confirmed the Rh(1.5) oxidation state assignment for the photosensitive "blue" species formed after the

evolution of one-half equivalent of hydrogen from $Rh_2b_4^{2+}$. The redox titrations also clarified the relationships among these and other oligomeric species of intermediate oxidation state. In association with the redox studies, mixtures of rhodium complexes both of "bridge" and of TMB (2,5-diisocyano-2,5-dimethylhexane) were prepared by direct reaction of $Rh_2(TMB)_4^{2+}$ with the "blue" solutions.[72] Among the species observed in both of these studies were (ligands omitted for clarity) Rh_4^{6+}, Rh_8^{10+} and Rh_{12}^{16+}. Finally, the tetranuclear structure for the "blue" complex was confirmed crystallographically.[73] It is now formulated as $Rh_4b_8^{6+}$, with one or two halides bound in equlibrium reactions. $Rh_2b_4^{4+}$ also binds halide ions, forming $Rh_2b_4X_2^{2+}$ species. Although the nature of the bound halide influences the electronic spectra somewhat,[71] in this discussion the halides have been omitted for simplicity.

The mechanism for hydrogen production in these systems is still not firmly established. The most direct evidence comes from flash kinetic spectroscopic studies of $Rh_4b_8^{6+}$. In H_2SO_4, as mentioned above, the principal photoreaction is homolytic cleavage, followed by rapid recombination:[69,70]

$$Rh_4b_8^{6+*} = 2\ Rh_2b_4^{3+} \qquad (10)$$

$$2\ Rh_2b_4^{3+} = Rh_4b_8^{6+} \qquad (11)$$

In hydrochloric acid similar reactions are observed,[74] but irreversible reactions occur as well. As reaction (10) in sulfuric acid appears not to lead to any net reaction, perhaps a new photoprocess occurs in aqueous HCl. One possibility is a disproportionation, or heterolytic cleavage:

$$Rh_4b_8^{6+*} = Rh_2b_4^{2+} + Rh_2b_4^{4+} \qquad (12)$$

The ultimate photooxidation product is $Rh_2b_4^{4+}$, and $Rh_2b_4^{2+}$ is already known to produce H_2:

$$2\ Rh_2b_4^{2+} + 2\ H^+ = Rh_4b_8^{6+} + H_2 \qquad (13)$$

Thus reaction (12) would provide a relatively simple explanation of the observed photochemistry. But the kinetics of the reactions actually observed are not so straightforward. Also, such a scheme merely defers the question of the hydrogen production mechanism to reaction (13)! Recent evidence indicates that hydride adducts of these binuclear isocyanides, originally proposed[68] for the photosensitive "blue" ion, can form;[75] such adducts may be intermediates in reaction (13).

The results presented herein address themselves to two goals. The first, mentioned above, is to understand the mechanism of the hydrogen-producing reactions. This inquiry comprises studies of the thermal reduction of $Rh_2b_4^{4+}$ by H_2 and of the photochemical oxidation of $Rh_4b_8^{6+}$ by O_2. The second group of experiments was designed to extend the photoredox chemistry observed[40] for $Rh_2b_4^{2+}$ and $Rh_2(TMB)_4^{2+}$ to aqueous solution, and to adapt these reactions to components of a water-splitting cycle.

B. EXPERIMENTAL

Rhodium complexes. The published procedure[67] was followed for preparation of $Rh_2b_4(BPh_4)_2.CH_3CN$. This was purified by recrystallization from acetonitrile before metathesis to other salts. Two methods were used to prepare $Rh_2b_4(BF_4)_2$. One was metathesis of the tetraphenylborate with Bu_4NBF_4 in acetonitrile. The other, originally developed by Lewis,[77] was more direct, precipitating the desired salt from an acetonitrile solution of $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ after treatment with $AgBF_4$.

Neither synthetic method for $Rh_2b_4(BF_4)_2$ afforded pure material, as evaluated by tests of hydrogen evolution.[78] Accordingly $Rh_2b_4(TFMS)_2$ was prepared by the following method, later reported in ref. 72. A solution of 10 g Bu_4NTFMS (Chapter II, section B) in 20 mL CH_3CN was added, with stirring, to a filtered solution of 0.32 g recrystallized $Rh_2b_4(BPh_4)_2$ in 300 mL CH_3CN. Gray needlelike crystals formed slowly, and the suspension was placed in the freezer overnight. Then the solid was collected, washed with ether and air-dried. Yield 0.23 g (95% if anhydrous) gray microcrystalline solid. IR: $\bar{\nu}$(CN) 2210 cm^{-1} (Nujol mull). Anal. Calcd. for $C_{22}H_{24}F_6N_8O_6Rh_2S_2$: C, 30.01; H, 2.75; N, 12.73. Found: C, 28.71; H, 2.77; N, 12.05. A dihydrate, although it would give better agreement with the analytical data, could be ruled out based on the IR spectrum (no absorption, 3050-3600 cm^{-1}).

Solid $Rh_2b_4(TFMS)_2$, the first crystalline salt of $Rh_2b_4^{2+}$ prepared without the acid-sensitive BPh_4^- ion, is sparingly soluble in acetonitrile and water and somewhat more soluble, especially on warming, in DMSO. Small needles were grown by slow evaporation of concentrated DMSO

solutions in air at 60 °C. Crystal faces parallel to the needle axis were strongly dichroic, opaque in parallel polarization and dark green in perpendicular polarization. The crystals were too small for a full crystallographic study, but precession photographs of one crystal showed orthorhombic symmetry, probably mm2 or mmm, with a = 23.9, b = 11.95 and c = 6.24 Å. Another crystal, used for oscillation and Weissenberg photographs, gave pseudotetragonal symmetry, a = 23.9, c = 6.24 Å. In addition, the odd-ℓ reflections were very weak, suggesting only a partial breakdown of symmetry from c = 3.12 A. Thus the most likely explanation is that the cations are stacked in the crystal, with the Rh-Rh axis parallel to c.

Solutions of $Rh_4b_8^{6+}$ in acidic solution were prepared by stirring $Rh_2b_4(BF_4)_2$ or $Rh_2b_4(TFMS)_2$ with the appropriate dilute acid (sulfuric or methanesulfonic) in air overnight and then filtering. These solutions were stable for several weeks and were diluted as needed for photochemical experiments. $[Rh_2b_4Cl_2]Cl_2.8H_2O$ was supplied by Dr. Kent R. Mann, and $[Rh_2b_4Br_2]Br_2.2H_2O$ was prepared by the photochemical method of Lewis.[77]

Other compounds. Except as noted, other compounds were reagent grade materials and were used as received. The method of Cooley and Yost[79] was used for $EuCO_3$, substituting Ar for CO_2 and without isolating the intermediate $EuSO_4$. Standard procedures were used for the air-stable $CrSO_4.5H_2O$[80] and for $H_2Co(EDTA).3H_2O$.[81] Other EDTA complexes were prepared in situ from $Fe(NH_4)_2(SO_4)_2.6H_2O$ and $(NH_4)Ti_3(SO_4)_5.9H_2O$. For the latter compound (also air-stable) the procedure of Stähler and Wirtwein[82] was used, except that their Ti(III) solution was duplicated

by Zn amalgam reduction of $TiOSO_4 \cdot 8H_2O$ in the same proportion of dilute H_2SO_4.

The macrocyclic compound $Co((CH_3)_6[14]dieneN_4)(ClO_4)_2 \cdot 2H_2O$[83] was supplied by Dr. Irving S. Sigal and recrystallized from water before use. TMPD (N,N,N′,N′-tetramethyl-1,4-benzenediamine) was either used directly as the free base (Aldrich; recrystallized before use and kept cold to inhibit air oxidation) or produced in a suitable buffer solution from its air-stable dihydrochloride (Eastman; recrystallized from 6 M HCl before use). Hydrochloric acid for kinetic studies (Section C) was ultrapure (G. F. Smith), diluted as needed with doubly deionized water.

Methods and instrumentation. Spectral measurements were made as in Chapter II, except that corrected emission spectra were recorded at UC Santa Barbara. Experiments with air-sensitive materials (such as Eu^{2+}) were conducted in buffered or strongly acidic aqueous solutions; the solid reductants (see above) were placed in a vacuum apparatus and the solution degassed in at least five freeze-pump-thaw cycles before mixing with the solids.

Analysis for hydrogen was conducted either using a Toepler pump (equipped with a heated CuO-filled tube for determining reducible gases by difference) or by an electrochemical method.[84] The potential applied to the hydrogen-sensitive electrode was adjusted to give approximately zero current, and variations in the current due to H_2 gas were recorded by means of a Keithley nanoammeter coupled to a y-t chart recorder. Calibrations were performed before and after each run using a gas-tight syringe and using the same current setting on the nanoammeter throughout. Typical sensitivity was 0.8-1.3 nA for a hydrogen pressure

of 1 mm Hg, or, for the vessel used in these experiments, a detection limit of less than 0.2 mL (8 μmole). The corresponding limit in the Toepler pump experiments was less than 0.1 mL (4 μmole). The amount of hydrogen expected on total consumption of the reducing agent was always at least five times the detection limit of the analyzing apparatus.

Quantum yields were determined by actinometry using tabulated quantum yields for aquation of Reinecke's salt.[85] Corrections were always made for thermal aquation ("dark" reaction). In these experiments a 200 W Hg(Xe) arc lamp, with Corning bandpass filters for 546 nm, served as the source. Qualitative photochemical experiments used the same lamp but with a ca. 450 nm cutoff filter.

C. KINETIC STUDIES AND QUANTUM YIELDS

As part of an effort to understand the photochemical formation of H_2 from $Rh_4b_8^{6+}$, it was of interest to examine the related thermal redox reactions in this system. Initial experiments indicated[68] that the yellow reaction product, $Rh_2b_4^{4+}$, reacted thermally with hydrogen to regenerate $Rh_4b_8^{6+}$. Richman and Mann observed[86] not only this reaction but also the reaction of $Rh_4b_8^{6+}$ itself with H_2, producing a gray species later identified by Sigal[72] as $Rh_6b_{12}^{8+}$. The studies reported herein were designed to continue those experiments.

Initial attempts in this investigation involved 1 M HCl solutions containing approx. 0.1 mM $Rh_2b_4^{4+}$. In the few cases where the reduction with H_2 appeared to proceed smoothly, the course of the reaction, monitored spectrophotometrically, was as follows: $Rh_2b_4^{4+}$ disappears, slowly at first, giving way to $Rh_4b_8^{6+}$. Gradually, as $Rh_2b_4^{4+}$ is depleted, the concentration of $Rh_4b_8^{6+}$ levels off, and absorption at 780 nm, attributable to $Rh_6b_{12}^{8+}$, can also be detected.

We had in mind a systematic study of the rates of these redox reactions. Particularly intriguing was the slow initial reduction of $Rh_2b_4^{4+}$ with H_2, suggesting that the reaction might be autocatalytic. Unfortunately, smooth reaction of the type described above occurred only in a few instances. Several experiments conducted in 1 M CH_3SO_3H with added NaBr also failed to give useful results. In HCl, reduction sometimes began before H_2 was added; in the bromide study the reduction rate varied significantly in different parts of the cell. Catalysis of the reduction by the cell surface or by some impurity on it seemed a likely cause, but new cells produced similar results. The hope of

obtaining quantitative information from these experiments was therefore abandoned.

Early in the investigation of the photochemical behavior of $Rh_4b_8^{6+}$ solutions, the quantum yield for the ion's photooxidaton was determined in a number of strong HCl solutions and in concentrated HBr.[87] Under these conditions H_2 is a significant photoproduct. In order to explore the details of these reactions, a study of quantum yields as a function of $[H^+]$ and $[X^-]$ was begun. This series of experiments was conducted in aerated dilute hydrohalic acid solutions, where O_2 (or possibly H_2O_2; see below) acts as oxidant. In all cases the progress of the photooxidation was monitored by the appearance of the intense $\sigma \rightarrow \sigma^*$ band in the $Rh_2b_4^{4+}$ product and was corrected for the relatively slow thermal oxidation.

The first group of experiments involved aerated 1 M CH_3SO_3H solutions with added NaBr. As the concentration of NaBr in the solution was increased from 0.005 M to 0.2 M, the photooxidation quantum yield more than doubled, from 0.008 to 0.020. Separate experiments demonstrated spectrophotometrically that association of Br^- with $Rh_4b_8^{6+}$ and $Rh_2b_4^{4+}$ was complete even at $[Br^-] = 0.0025$ M. Thus free Br^- apparently enhances the photochemical reaction rate. This observation is consistent with a scheme beginning with heterolytic cleavage (reaction (12)), in which the binding of a (second) halide to $Rh_2b_4^{4+}$ might compete effectively with recombination and allow $Rh_2b_4^{2+}$ to react further.

The influence of oxygen pressure was the second topic of investigation. Here all solutions were 1 M in HCl, and measured mixtures of N_2 and O_2 (or N_2 and air) were bubbled through the solutions during irradiation. This time the quantum yields varied only irregularly for O_2

partial pressures up to 1 atm; moreover, there was significant photooxidation ($\Phi \sim 0.02$) when pure N_2 was used!

This result can be interpreted in two ways. One is that the solutions always contained O_2, either because the degassing procedure was inadequate or because the N_2 reaching the cuvette was no longer pure. This is unlikely, as the wide range of measured O_2 partial pressures should have caused at least some consistent variation in Φ. As an additional test, a $Rh_4b_8^{6+}$ solution in 1 M HCl was freeze-pump-thaw degassed; subsequent irradiation under the usual conditions resulted in clean oxidation to $Rh_2b_4^{4+}$.

The second possibility is that the solutions contain a substance which photooxidizes $Rh_4b_8^{6+}$ and is not removed by degassing. This proposal brings up the question of how $Rh_4b_8^{6+}$ is formed when $Rh_2b_4^{2+}$ dissolves in acidic solution. Sigal and co-workers showed[71] that hydrogen is evolved (reaction (13)) when the process occurs in degassed concentrated HCl. In addition, though, their studies suggest that the aerial oxidation of $Rh_2b_4^{2+}$ in dilute acidic solution also produces H_2O_2. Thus solutions of $Rh_4b_8^{6+}$ prepared in air, when titrated immediately, require 4 equivalents of Ce(IV) for complete oxidation to $Rh_2b_4^{4+}$.

If H_2O_2 is produced stoichiometrically in these reactions of $Rh_2b_4^{2+}$ in aerated acidic solution, the concentrations of dissolved H_2O_2 will be comparable (even if the solution is in equilibrium with pure O_2) and thus the two substances might well compete in the photooxidation of $Rh_4b_8^{6+}$.

D. EXCITED STATE REDOX REACTIONS

Milder and co-workers first established[40] that the low-lying $^3A_{2u}$ excited states of $Rh_2b_4^{2+}$ and $Rh_2(TMB)_4^{2+}$ could undergo redox reactions with various donors and acceptors. They were able to set limits on the redox properties of the excited states. The modified Latimer diagram for $Rh_2b_4^{2+}$ in Figure 16(a), for example, is derived from these data and from the electrochemical studies of Najdzionek.[88] The powerfully reducing nature of the two Rh_2^+ ions produced in these experiments suggests that, if generated in aqueous systems, they might be capable of reducing water or H^+ to hydrogen. Most of the experiments previously described involving photogenerated reductants[6] have required added heterogeneous catalysts. However, as $Rh_2b_4^{2+}$ was already known to produce H_2 on reaction with strong acids, it seemed likely that the reduction in this case might proceed in homogeneous solution. The experiments described here were designed to examine this possibility, while exploring in more detail the relationships among these ions in aqueous solution.

Initial experiments were conducted in a glass apparatus equipped for passage of inert gas and analysis of the hydrogen present by an electrode sensitive to H_2 gas.[84] These were designed to take advantage of the following sensitized reduction of H^+ by an electron donor D:

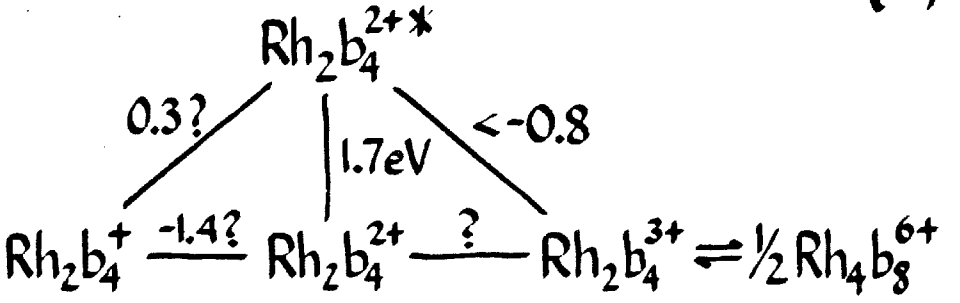
$$Rh_2b_4^{2+*} + D = Rh_2b_4^{+} + D^+ \qquad (14)$$

$$Rh_2b_4^{+} + H^+ = Rh_2b_4^{2+} + 1/2\ H_2 \qquad (15)$$

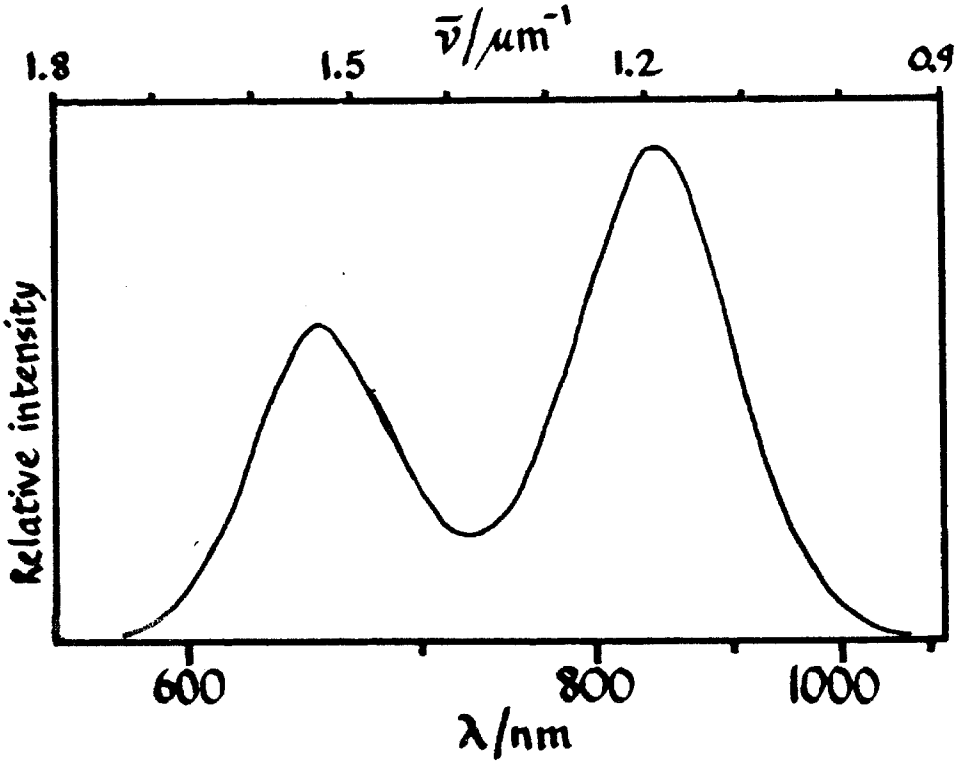
Although one of these trial experiments, in 1 M CH_3SO_3H with electrochemically generated Eu^{2+} as donor, had been reported to give a

Figure 16. (a) Modified Latimer diagram for $Rh_2b_4^{2+}$ in acetonitrile, from data in refs. 40 and 88 (electrode potentials/V vs. SCE). (b) Corrected emission spectrum for $Rh_2b_4^{2+}$ in methanol-water (2:1) at room temperature. Excitation wavelength 546 nm.

(a)


$Rh_2b_4^{2+*}$
0.3?
1.7eV
<-0.8
$Rh_2b_4^{+}$
-1.4?
$Rh_2b_4^{2+}$
?
$Rh_2b_4^{3+}$
$\rightleftharpoons \frac{1}{2} Rh_4b_8^{6+}$

(b)


$\bar{\nu}/\mu m^{-1}$
1.8
1.5
1.2
0.9
Relative intensity
600
800
1000
λ/nm

yield of H_2,[89] I was unable to duplicate that result with $EuCO_3$. Similar attempts with Cr^{2+} and Fe^{2+}, the latter more ambitious in terms of the energetics of reaction (14) but still within the limits of the modified Latimer diagram, were also unsuccessful. In further trials standard vacuum apparatus was used and hydrogen determined via Toepler pump collection for two reasons: rigorous exclusion of air was relatively easy, and absorption spectra of the solutions could be recorded during the experiments. Both with $Rh_2b_4^{2+}$ and $Rh_2(TMB)_4^{2+}$ as chromophore, H_2 evolution from Eu^{2+} proceeded at a significant rate even in the dark and was at most slightly accelerated under irradiation.

An additional attempt to sensitize the evolution of H_2 from these solutions involved $Rh_2(TMB)_4^{2+}$ as chromophore, with Eu^{2+} donor and the macrocyclic Co(II) complex $Co((CH_3)_6[14]dieneN_4)^{2+}$ (CoL^{2+}). Sutin and co-workers, recognizing that the powerful reductant CoL^+ was already known[90] to react with H^+, produced it using photochemically generated $Ru(bpy)_3^+$ and thereby sensitized the reduction of H^+ to H_2 by Eu^{2+} or ascorbic acid in homogeneous solution.[91] The experiment conducted here, however, gave no evidence of accelerated hydrogen production under irradiation. It might also be noted that a reaction of $Rh_2b_4^+$ with H^+ similar to that of CoL^+,

$$Rh_2b_4^+ + 2\ H^+ = Rh_2b_4^{3+} + H_2, \qquad (16)$$

while possible as an alternative to (15) and thermodynamically favorable according to the modified Latimer diagram, apparently does not proceed either.

At about this time the redox relationships among the various Rh_2b_4 oligomers were being clarified. The acidic solutions prepared from

$Rh_2b_4(TFMS)_2$ displayed the characteristic pink color of aqueous $Rh_2b_4^{2+}$ as long as excess reductant (e.g. Eu^{2+}) was present. However, as H_2 was gradually evolved, consuming the Eu^{2+}, the pink color faded, and slowly the violet color of $Rh_4b_8^{6+}$ developed. It appeared, therefore, that $Rh_2b_4^{2+}$ was a convenient thermal catalyst for the reduction of H^+ by Eu^{2+}! The sensitivity of $Rh_2b_4^{2+}$ to oxidation even in relatively dilute acid solutions had been noted before in the quantum yield studies of section C. These results are in agreement with those of Sigal, Mann and Gray,[71] who found that, in dilute H_2SO_4, $Rh_2b_4^{2+}$ could only be prepared in the presence of a large excess of reductant (Cr^{2+} in their case).

The stability of $Rh_2b_4^{2+}$ in water (see section B) and its decomposition in acidic solution are best reconciled by the change in the hydrogen electrode potential with pH. Additional experiments were therefore conducted in various buffer solutions (most often an acetate buffer, pH 5.4, or a borate buffer, pH 8.6). In degassed solution under these conditions $Rh_2b_4^{2+}$ was stable for extended periods of time.

Experiments with $Rh_2b_4^{2+}$ in these buffer solutions utilized EDTA complexes of Fe^{2+}, Co^{2+} and Ti^{3+} as potential electron donors of progressively greater reducing power (E^o/V vs. NHE, 0.38,[92] 0.12[93] and -0.2[94] under these conditions). None of these experiments gave evidence for permanent oxidation of the metal-EDTA complexes or for reduction of H^+. At this point it appeared that there might be a flaw in the reasoning behind reactions (14) and (15). Specifically, the high-spin EDTA complexes used might quench $Rh_2b_4^{2+*}$ by energy transfer. To test this hypothesis, experiments with the donors $Ti(EDTA)^-$ and TMPD were assembled for both emission spectra and flash photolysis. Both donors quenched the $Rh_2b_4^{2+}$ phosphorescence (Figure 16(b)), but only the TMPD

trial gave transient absorptions attributable to $Rh_2b_4^+$ (430 and 710 nm[40]) and $TMPD^+$ (610 nm[95]). Finally, having shown at least that TMPD caused reductive quenching of $Rh_2b_4^{2+}*$ in the aqueous buffer, I attempted to use it as donor in reactions (14) and (15). This experiment also failed.

E. PROSPECTS

Early studies of $Rh_2b_4^{2+}$ and its derivatives demonstrated a rich photoredox chemistry. The tetranuclear $Rh_4b_8^{6+}$ complex in particular produces hydrogen from homogeneous strongly acidic solution when irradiated. Additional experiments focused on the redox reactions of the lowest triplet excited state of the parent $Rh_2b_4^{2+}$ ion. The experiments described herein dealt with two aspects of these reactions: First, thermal and photochemical redox reactions were explored for the $Rh_4b_8^{6+}$ - $Rh_2b_4^{4+}$ system in dilute acid solution. Second, I attempted to bring together the photoinduced electron transfer and thermal hydrogen production reactions into a single system for truly photocatalytic hydrogen evolution from mild reductants. Although the first set of experiments was only partially successful, and the second group did not achieve its objective of hydrogen production, some general conclusions can be reached because both studies examined similar types of reactions.

In the photochemical studies of oxidation of $Rh_4b_8^{6+}$, the overall yield of photooxidation products increases with $[Br^-]$. If a disproportionation process such as (12) is actually involved in the photooxidation, this behavior might be expected if a halide ion "traps" $Rh_2b_4^{4+}$. Thus Br^- may inhibit direct recombination of the disproportionation products. The bimolecular reactions of section D were essentially a similar attempt to inhibit recombination, this time in reaction (14). This time the inhibition was to take place by rapid evolution of hydrogen from $Rh_2b_4^{+}$ (or a species made from it). Considering that most reactions involving strongly bound gases such as H_2 proceed at low rates

without heterogeneous catalysts, the failure here is perhaps not so surprising.

There is still room for significant progress in the study of these photoredox reactions. Although the excited state electron transfer reactions first documented for $Rh_2b_4^{2+}$ now seem common to a number of binuclear d^8 systems, the homogeneous reactions leading to reduction of H^+ are still unique to $Rh_2b_4^{2+}$. Additional exploration of those reactions might give useful information, but such studies will be difficult because the reactions are so sensitive to impurities.[74] A promising avenue is the recent work of Smith[75] with hydrides formed from various Ir and Rh isocyanides. Even though the photochemically active solutions prepared from $Rh_2b_4^{2+}$ were recently shown to contain $Rh_4b_8^{6+}$ and not a hydride such as $(HRh_2b_4^{3+})_n$, such hydrides do form. They may well serve as intermediates in the hydrogen-producing reactions; their chemistry is only now beginning to be explored.

APPENDICES

APPENDIX I. MAGNETIC SUSCEPTIBILITY OF $(Bu_4N)_2Mo_6Cl_{14}$

The magnetic susceptibility of a powdered sample of $(Bu_4N)_2Mo_6Cl_{14}$ has been determined at temperatures between 2 and 300 K. The measurements were made in collaboration with Dr. Richard Dee of S. H. E. Corporation, San Diego, CA 92121, and utilized their model 805 Variable Temperature Susceptometer with low-temperature option.

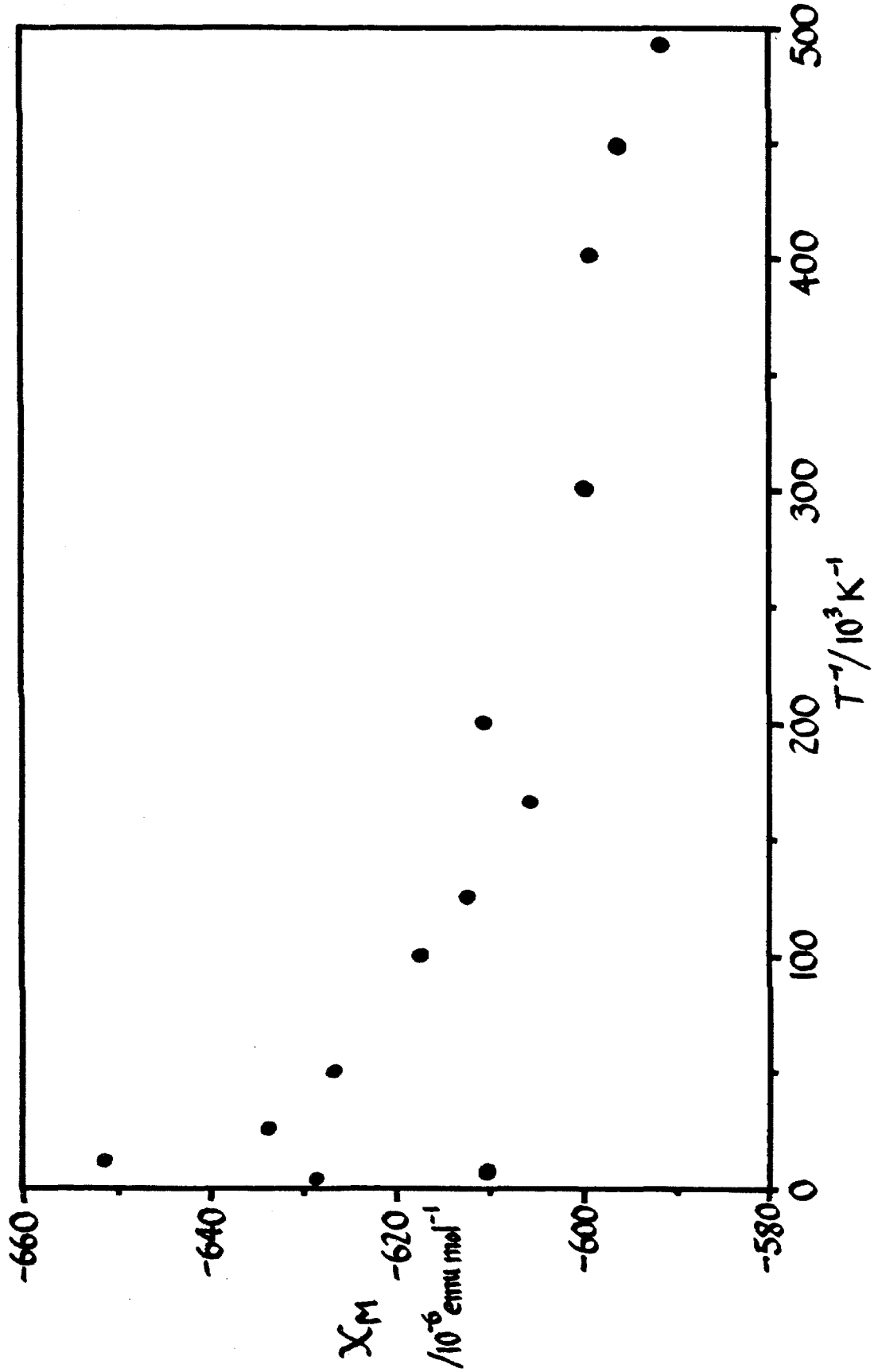
Powdered $(Bu_4N)_2Mo_6Cl_{14}$ (0.0574 g; 3.69×10^{-5} mole) was placed in an aluminum-silicon alloy sample holder (mass 0.0943 g), suspended by a short length of fine copper wire and by a longer cotton thread, and measurements made on it. Later the sample was removed and the measurements repeated at the same temperatures with the sample holder, wire and thread only. The output of the SQUID-based susceptometer is a signed voltage based on peak-to-peak measurements of the signal as the sample is passed between two sensing coils. Sequential readings for upward and downward movement of the sample were averaged, and between three and fifteen such pairs of measurements were averaged to give the "magnetic moments" listed in Table 4. The net "magnetic moment" was obtained by subtraction and converted into the molar susceptibility χ_M via the magnetic field strength (10^4 G = 1 T throughout).

The data for χ_M as a function of 1/T are plotted in Figure 17. As these show a relatively large amount of scatter, a word about measurement accuracy may be helpful. At any given temperature, individual pairs of measurements were usually within 1% of one another. Some pairs fell well outside this tolerance and were discarded. Thus the net "magnetic moments" are probably accurate to approx. 1.3×10^{-5} emu, leading to an uncertainty in χ_M of some 35×10^{-6} emu mol^{-1}. Thus the minor

Table 4. Magnetic susceptibility data for powdered $(Bu_4N)_2Mo_6Cl_{14}$.

T/K	T^{-1} /$10^{-3}K^{-1}$	"Moments"/10^{-4}emu Holder + sample	Holder only	Net	χ_M /10^{-6}emu mol^{-1}
300	3.3	4.683	7.001	-2.318	-629
150	6.7	5.275	7.525	-2.250	-610
90	11.1	5.292	7.693	-2.401	-651
40	25.0	5.466	7.803	-2.337	-634
20	50.0	5.529	7.840	-2.311	-627
10	100.0	5.613	7.889	-2.276	-617
8	125.0	5.656	7.913	-2.257	-612
6	166.7	5.715	7.948	-2.233	-606
4.99	200.4	5.715	7.966	-2.251	-610
3.32	301.2	5.820	8.032	-2.212	-600
2.49	401.6	5.909	8.118	-2.209	-599
2.23	448.4	5.958	8.156	-2.198	-596
2.04	492.6	5.988	8.169	-2.181	-592

Figure 17. Magnetic susceptibility of powdered $(Bu_4N)_2Mo_6Cl_{14}$ as a function of reciprocal temperature.


-660
-640
-620
-600
-580
χ_M /10^{-6} emu mol^{-1}
0
100
200
300
400
500
$T^{-1}/10^3 K^{-1}$

variations observed in Figure 17 are, except for those at the highest temperatures, well within this limit. It was apparent from the raw data that the readings at higher temperatures were more frequently in error; this, combined with the more rapid change of the sample holder's "moment" with 1/T, probably accounts for their greater scatter. Within the accuracy of the measurements, the calculated susceptibility becomes slightly more negative at high temperatures. In any case the susceptibility of ca. -630×10^{-6} emu mol^{-1} is considerably greater (more positive) than that (-760×10^{-6} emu mol^{-1}) expected from just C, H, N and Cl.[96] See chapter II, section C for further discussion.

APPENDIX II. STRUCTURAL STUDIES OF RHODIUM AND IRIDIUM ISOCYANIDES

In this section the crystal structure analysis of $[Rh_2(TMB)_4Cl_2](PF_6)_2$ is summarized, and geometrical details of the Rh cation are compared with those of related polynuclear isocyanide complexes in the literature. Some generalizations are noted concerning metal–metal distance, rotation of the $M(C)_4$ planes about the M–M bond, and deformations of the ligand molecules in both bridged and unbridged structures.

Crystal data. $[Rh_2(TMB)_4Cl_2](PF_6)_2$, M_r 1223.64, a = 13.846(5), b = 24.773(3), c = 17.068(4) Å, V = 5854.4 Å^3, D_c = 1.39 for Z = 4, D_m = 1.37(1); space group Pbcn. A small (all dimensions < 0.1 mm) crystal was supplied by Dr. Vincent M. Miskowski. An Enraf–Nonius CAD4 diffractometer fitted with Mo source and graphite monochromator for MoK radiation was used to collect data for 4573 unique reflections (+h, +k, +ℓ) with $0.1^\circ < \theta < 23^\circ$. Systematic absences in the diffraction data suggested the space group Pbcn.

Solution and refinement. The SHELX[97] system of programs was used to solve the structure by direct methods. The initial solution for the Rh and Cl atoms was checked against the Patterson map. These positions were used in three Fourier syntheses, after which all atoms other than hydrogen had been located. The structure was refined in several stages: first with only Rh, Cl, P and F anisotropic, and second with all non-H atoms anisotropic, with unit weights and riding H atoms throughout. Subsequent refinement was carried out with $1/\sigma$ weighting, exploring the possibility of disorder in two of the TMB methyl groups. Final R_w was

ca. 0.08 depending on the model and the number of reflections used. In most of the later stages the structure was refined in blocks, largely to circumvent program size limitations.

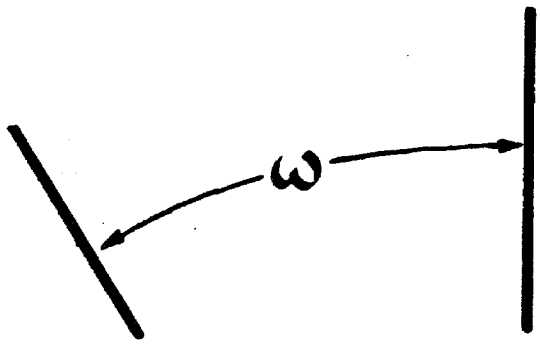
A drawing of the Rh cation, prepared using the program ORTEP,[98] appears in Figure 18. The two methyl carbon atoms with the most eccentric ellipsoids are those for which a disorder model was examined.

Structural data. The Rh cation lies on a site of crystallographic C_2 symmetry. The Rh-Rh and Rh-Cl distances are respectively 2.770(3) and 2.428(6) Å. Other distances and angles, as well as the PF_6^- parameters, are in reasonable agreement with expected values; but in the ligand where disorder appears to be present, the deviations are significantly larger. The two $Rh(C)_4$ planes are essentially parallel, and the staggering angle ω (the smallest C-Rh-Rh-C torsion angle) is 32°.

Discussion. The original reason for solving the structure of $[Rh_2(TMB)_4Cl_2](PF_6)_2$ was to provide orientation data for an optical spectroscopic study: the molecules are closely aligned with the c axis. In the process, however, we grew interested in some of the features of the cation's geometry and in how they might relate to the corresponding properties of other polynuclear isocyanide complexes. Figure 19 gives cross-sections from crystallographic data for this and other complexes.

In complexes of "bridge" (Fig. 19(a)), both the Rh(I)[76] and Rh(II)[99] forms are eclipsed, and the smallest deviations from ideal Rh-Rh-C and Rh-C-N angles are in the Rh(II) ion. The TMB complexes in (b) (this work and ref. 76) and (c)[100] are both staggered, and this time the strain seems less serious in Rh(I). The Rh(II) and Ir(II) structures appear quite similar. The Rh(I) complex[101] of DMB (1,8-diisocyano-p-

Figure 18. ORTEP[98] drawing of the $Rh_2(TMB)_4Cl_2^{2+}$ ion. Hydrogen atoms omitted for clarity.


ω

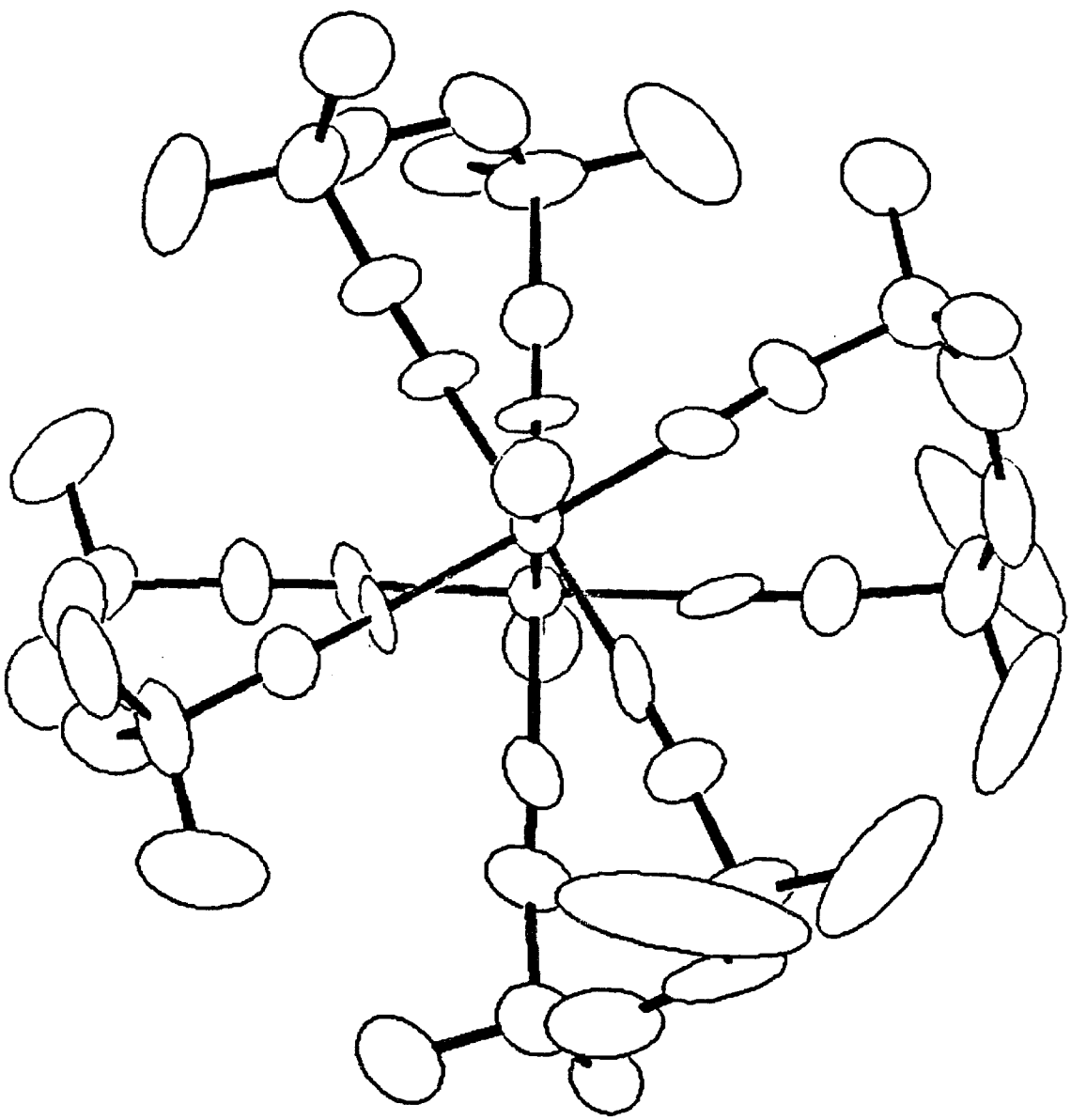
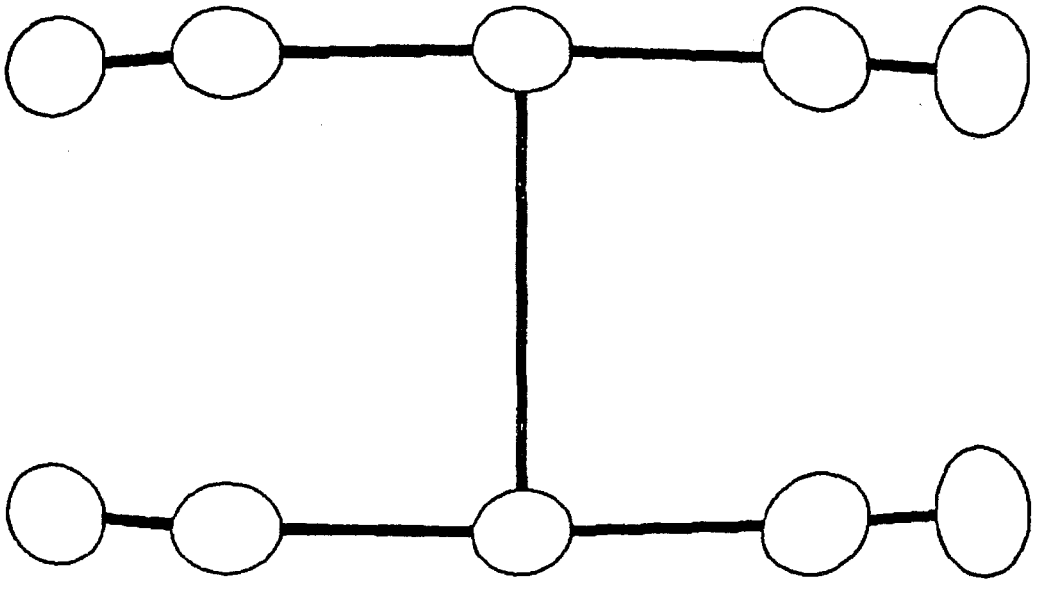
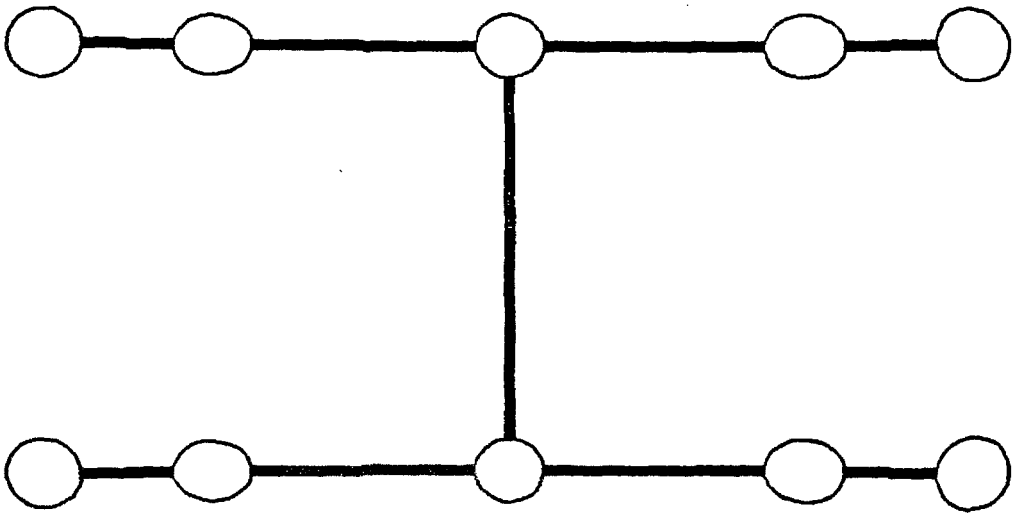


Figure 19. Cross-sections of polynuclear isocyanide cations. Individual formulas given, and metal–metal distances and staggering angles listed, on each illustration. See text for references.

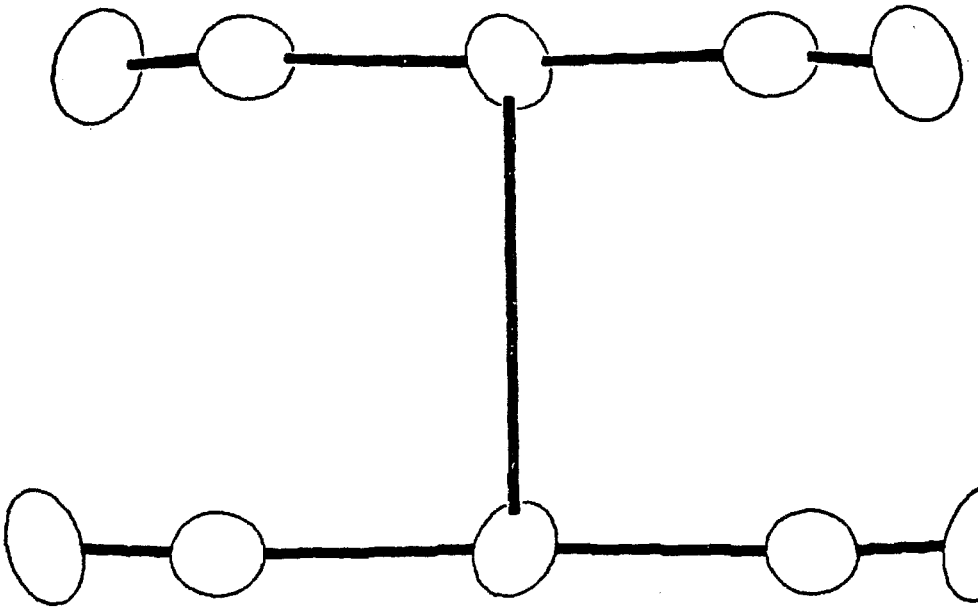


$Rh_2(bridge)_4^{2+}$ $\omega = 0°$ 3.24 Å

(a)

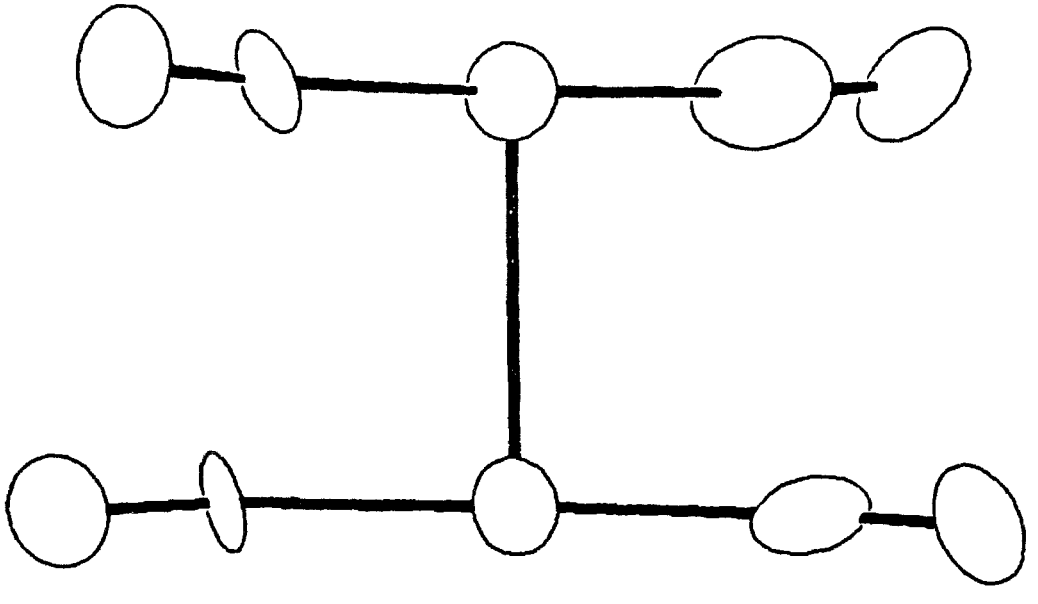


$Rh_2(bridge)_4^{4+}$ $\omega = 0°$ 2.84 Å

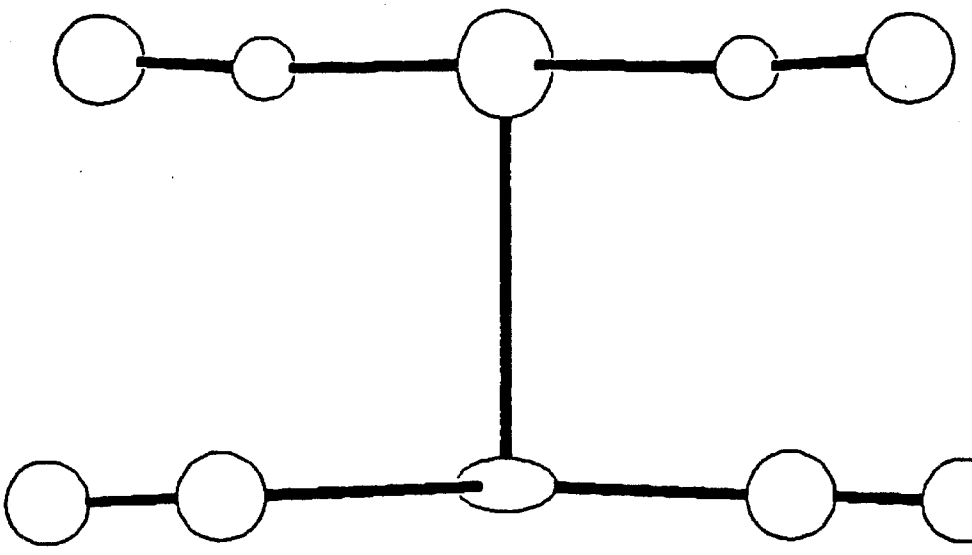


$Rh_2(TMB)_4^{2+}$ $\omega \sim 25°$ 3.26 Å

(b)

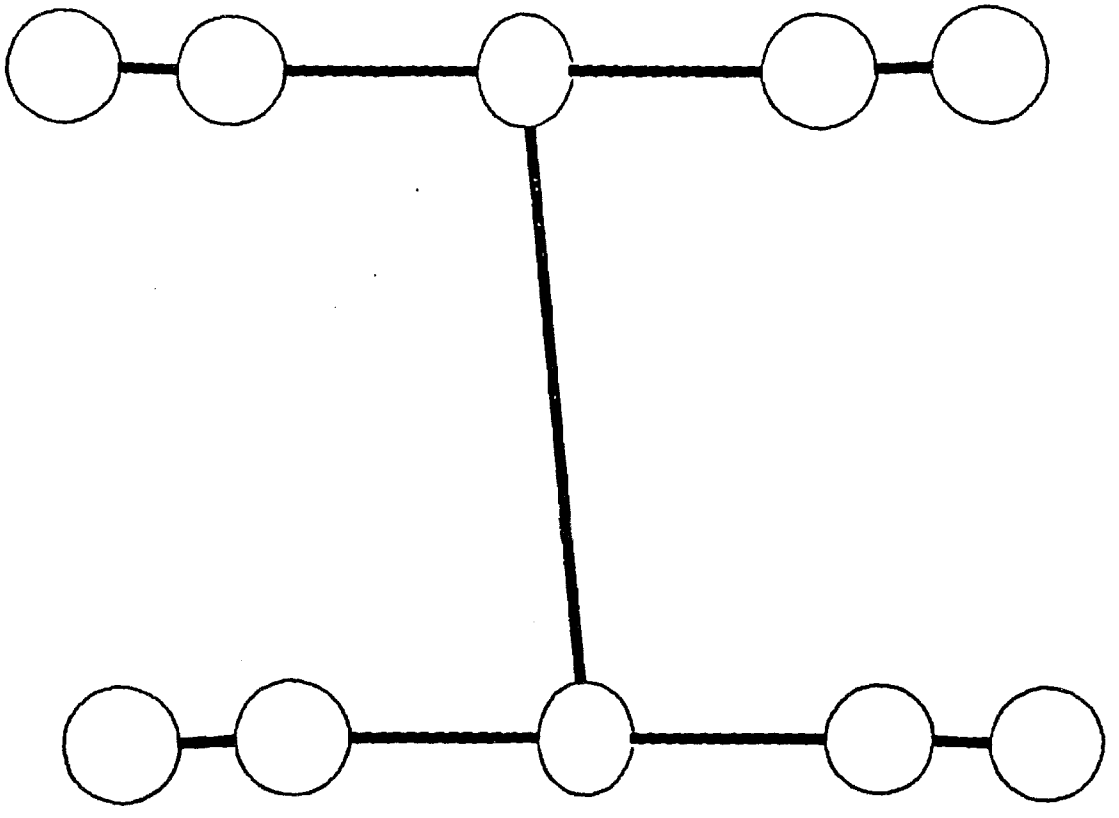


$Rh_2(TMB)_4^{4+}$ $\omega = 32°$ 2.77 Å

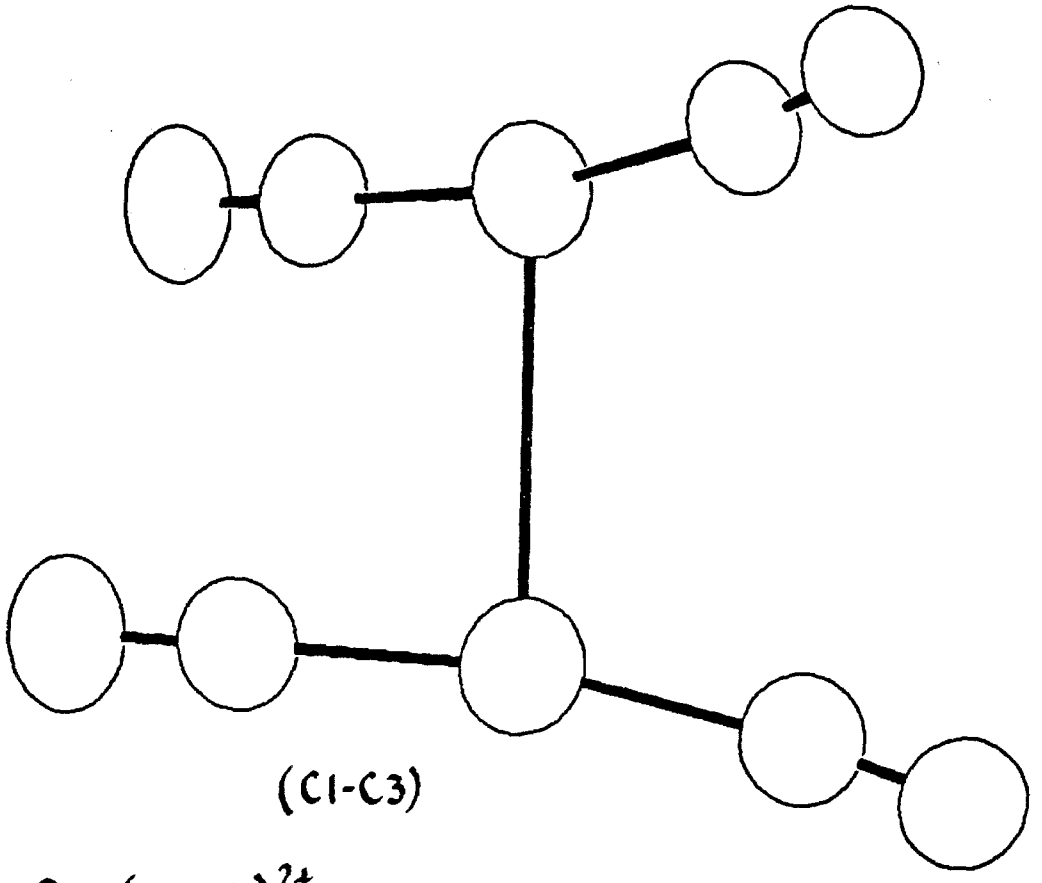


$Ir_2(TMB)_4^{4+}$ $\omega = 31°$ 2.82 Å

(c)



$Rh_2(DMB)_4^{2+}$ $\omega = 0°$ 4.48 Å

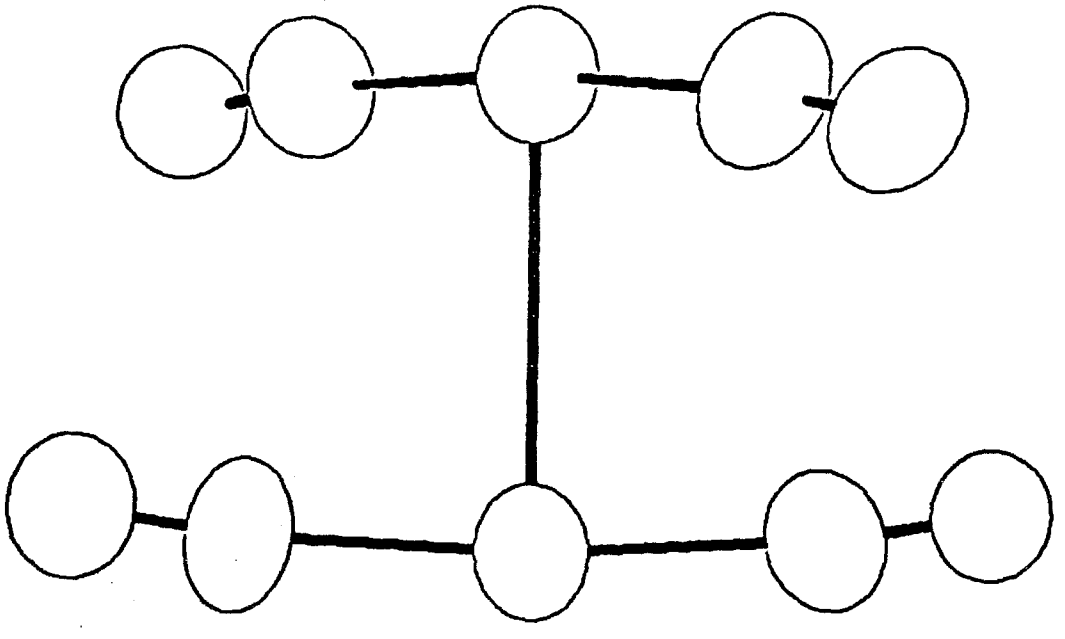


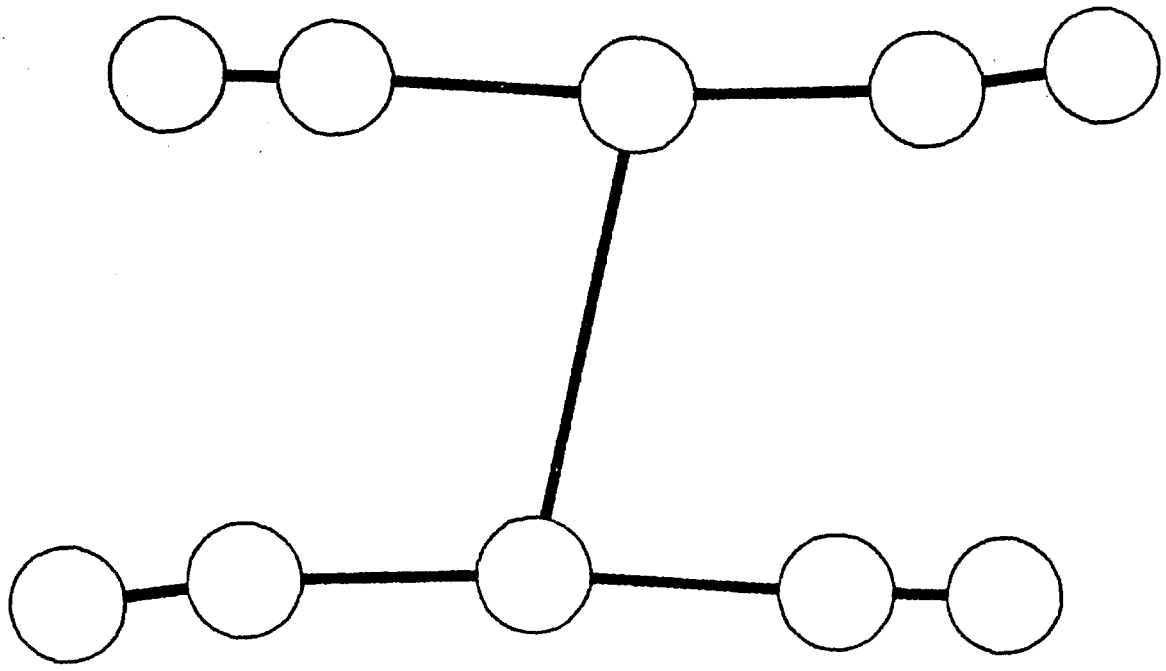
(C1-C3)

$Rh_2(CNPh)_8^{2+}$ $\omega \sim 40°$ 3.19Å

(d)

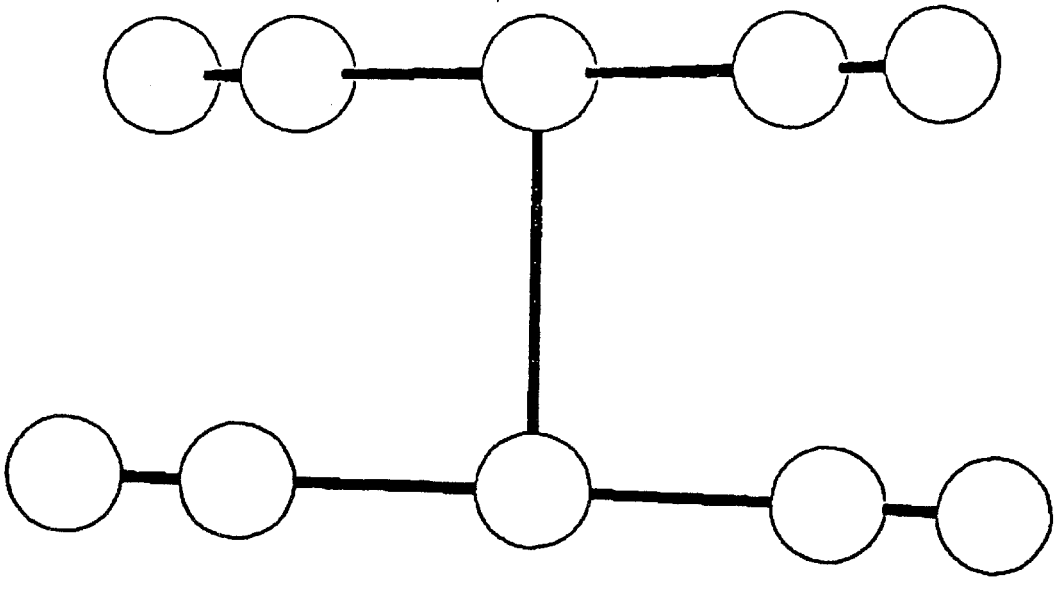
(C2-C4)



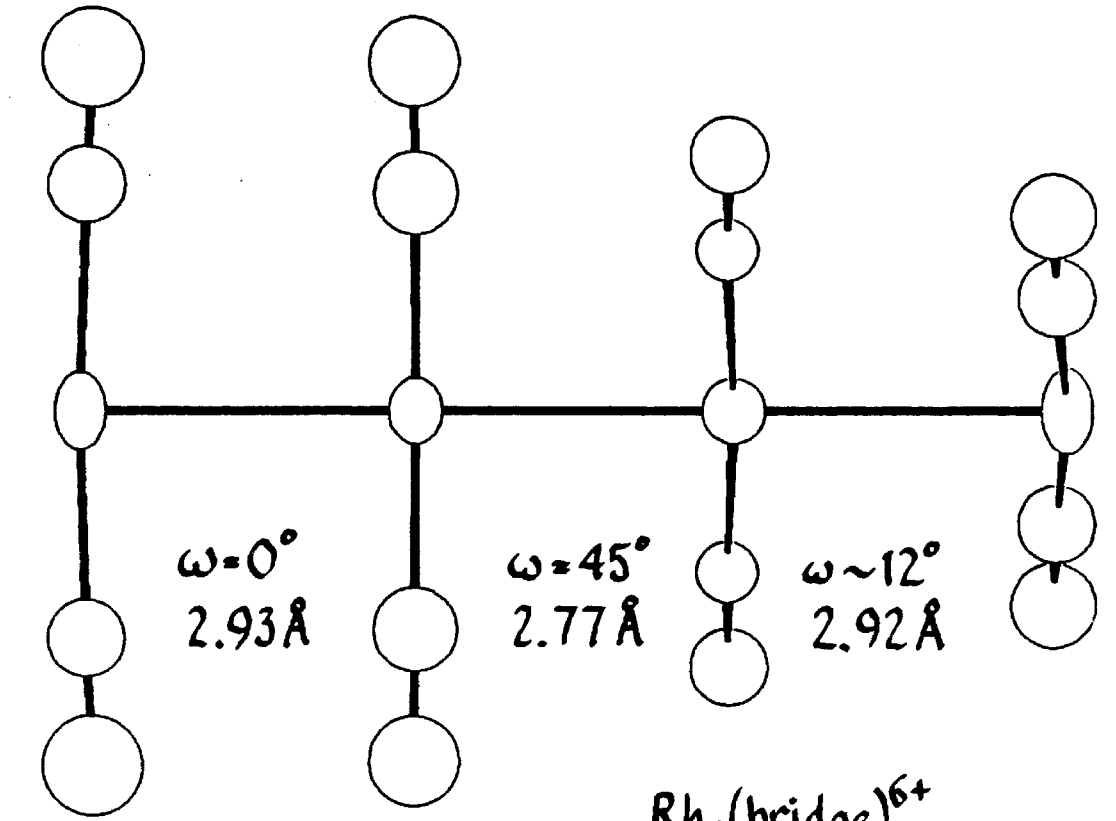


$Rh_2(CNC_6H_4\text{-}p\text{-}F)_8^{2+}$ $\omega = 2°$ 3.21 Å

(e)

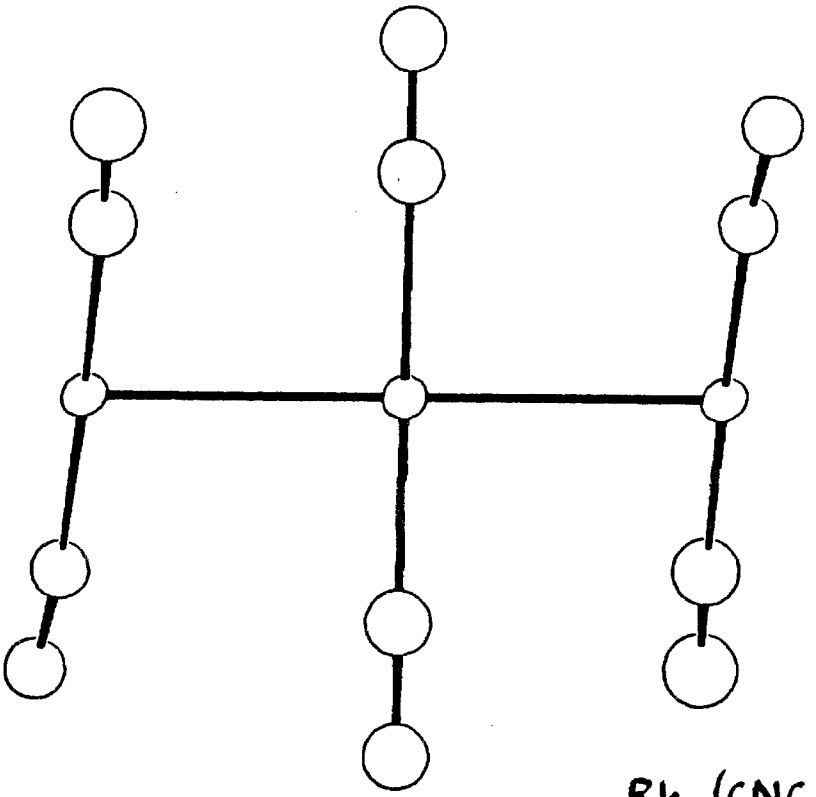


$Rh_2(CNC_6H_4\text{-}p\text{-}CH_3)_8^{4+}$ $\omega \sim 30°$ 2.79 Å



$Rh_4(bridge)_8^{6+}$

(f)



$Rh_3(CNCH_2Ph)_{12}^{5+}$

menthane) (c) shows that the weak Rh-Rh attraction can easily be overcome by a rigid ligand.

We had hoped that the geometric parameters in the bridged complexes could be correlated with those for unbridged species. The geometry of $Rh_2(CNPh)_8^{2+}$ (Fig. 19(d), two projections),[66] however, shows striking departures from ideal shape. Here the Rh-Rh-C angles are 87°, 87°, 88° and 103°! In $Rh_2(CNC_6H_4\text{-}p\text{-}F)_8^{2+}$ (e)[102] the ligands are eclipsed but the planes are no longer perpendicular to the Rh-Rh vector. Distortions in $Rh_2(CNC_6H_4\text{-}p\text{-}CH_3)_8I_2^{2+}$,[103] on the other hand, appear relatively minor.

Finally two other structures are included (Fig. 19(f)), of the photosensitive $Rh_4b_8^{6+}$ ion,[73] and of the novel trinuclear species $Rh_3(CNCH_2Ph)_{12}I_2^{3+}$. The first is of interest in that one Rh_2b_4 moiety is staggered ($\omega \sim 12°$); and in the second, the outer ligands can be seen to bend away from the relatively undistorted central plane.

In general, the bridging ligands appear to enforce a geometrical regularity not demanded of the unbridged structures. Although the data do not permit strong generalizations, some conclusions can be drawn. While the relatively compact "bridge" ligand suffers less distortion in its Rh(II) complex than in Rh(I), the opposite seems true of TMB. Staggering angles tend to be larger in Rh(II) and Ir(II) structures than in Rh(I). Also, the wide variety among the unbridged structures suggests that packing forces, either among the ligands or between the ligands and counterions, can easily surpass the electronic forces associated with bending bonds to the metal atom. Thus the geometric preferences immediately surrounding the metal atoms, although possibly controlling in the limiting case of bridging ligands, are actually slight.

REFERENCES

(1) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press, London, 1970.

(2) Bock, C. R.; Koerner von Gustorf, E. A. Advan. Photochem. 1977, 10, 221-310.

(3) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press, New York, 1979.

(4) Adamson, A. W.; Fleischauer, P. D. (eds.) "Concepts of Inorganic Photochemistry"; Wiley-Interscience, New York, 1975.

(5) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. Coord. Chem. Rev. 1975, 21, 321-433; Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. Topics Curr. Chem. 1978, 78, 1-64.

(6) Maverick, A. W.; Gray, H. B. Pure Appl. Chem. 1980, 52, 2339-2348.

(7) Heidt, L. G.; Mullin, M. G.; Martin, W. B., Jr.; Beatty, A. M. J. J. Phys. Chem. 1962, 66, 336-341; Jortner, J.; Stein, G. J. Phys. Chem. 1962, 66, 1258-1264; 1264-1271.

(8) Gafney, H. D.; Adamson, A. W. J. Am. Chem. Soc. 1972, 94, 8238-8239.

(9) Blömstrand, W. J. Prakt. Chem. 1859, 77, 88-119. Molybdenum dichloride had probably been made before (see this paper; also Svanberg, L.; Struve, H. Phil. Mag. 1848, 33, 524-546, and references therein), but Blömstrand's work began to set the stage for its recognition as a cluster species.

(10) Roscoe, H. E. Ann. 1872, 162, 349-368.

(11) Rosenheim, A.; Kohn, F. Z. Anorg. Chem. 1910, 66, 1-6.

(12) Brosset, C. Arkiv Kemi, Min. Geol. 1945, 20A, No. 7 (16 pp.)

(13) Brosset, C. Arkiv Kemi, Min. Geol. 1947, 25A, No. 19 (14 pp.)

(14) Vaughan, P. A. Proc. Nat. Acad. Sci. U. S. A. 1950, 36, 461-464.

(15) Schäfer, H.; von Schnering, H.-G.; Tillack, J.; Kuhnen, F.; Wöhrle, H.; Baumann, H. Z. Anorg. Allg. Chem. 1967, 357, 281-310.

(16) The molybdenum halides are most conveniently prepared by reduction of Mo(III) and other higher halides: Jödden, K.; Schäfer, H. Z. Anorg. Allg. Chem. 1977, 430, 5-22; or by comproportionation, according to the method of ref. 17 or as in Koknat, F. W.; Adaway, T. J.; Erzerum, S. I.; Syed, S. Inorg. Nucl. Chem. Lett. 1980, 16, 307-310. For the preparation of the tungsten halides see ref. 18.

(17) Nannelli, P.; Block, B. P. Inorg. Chem. 1968, 7, 2423-2426.

(18) Hogue, R. D.; McCarley, R. E. Inorg. Chem. 1970, 9, 1354-1360.

(19) Cotton, F. A.; Curtis, N. F. Inorg. Chem. 1965, 4, 241-244.

(20) Sheldon, J. C. J. Chem. Soc. 1960, 1007-1014.

(21) Sheldon, J. C. J. Chem. Soc. 1962, 410-415.

(22) Hamer, A. D.; Smith, T. J.; Walton, R. A. Inorg. Chem. 1976, 15, 1014-1017.

(23) Kepert, D. L.; Marshall, R. E.; Taylor, D. J. Chem. Soc. Dalton Trans. 1974, 506-509.

(24) Gibson, J. F.; Meier, P. O. W. J. Chem. Res. Synop. 1978, 66-67. J. Chem. Res. Miniprint 1978, 946-956.

(25) Siepmann, R.; von Schnering, H.-G.; Schäfer, H. Angew. Chem. Int. Ed. Engl. 1967, 6, 637.

(26) Schäfer, H.; Siepmann, R. Z. Anorg. Allg. Chem. 1968, 357, 273-288.

(27) Siepmann, R.; von Schnering, H.-G. Z. Anorg. Allg. Chem. 1968, 357, 289-298.

(28) Lindner, K.; Haller, E.; Helwig, H. Z. Anorg. Allg. Chem. 1923,

130, 209-228.

(29) Le Berre, A.; Étienne, A.; Dumaitre, B. Bull. Soc. Chim. Fr. 1970, 954-958. The previously unreported BSPP has recently been described, but without synthetic details: Willner, I.; Otvos, J. W.; Calvin, M. J. Am. Chem. Soc. 1981, 103, 3203-3205.

(30) Sultones have been used before as sulfoalkylating agents: Helberger, J. H.; Manecke, G.; Heyden, R. Justus Liebigs Ann. Chem. 1949, 565, 22-35.

(31) Bird, C. L.; Kuhn, A. T. Chem. Soc. Rev. 1981, 10, 49-82.

(32) Kosower, E. M.; Cotter, J. L. J. Am. Chem. Soc. 1964, 86, 5524-5527.

(33) Wu, H. J. Biol. Chem. 1920, 43, 189-220.

(34) Prados, R. A.; Pope, M. T. Inorg. Chem. 1976, 15, 2547-2553.

(35) Brändström, A.; Berntsson, P.; Carlsson, S.; Djurhuus, A.; Gustavii, K.; Junggren, U.; Lamm, B.; Samuelsson, B. Acta Chem. Scand. 1969, 23, 2002.

(36) Wilson, W. L. British Patent #739,144. See C. A. 1956, 50, 10354a.

(37) Parker, C. A.; Rees, W. T. Analyst 1960, 85, 587-600.

(38) Van Houten, J.; Watts, R. J. J. Am. Chem. Soc. 1976, 98, 4853-4858.

(39) Watts, R. J.; Van Houten, J. J. Am. Chem. Soc. 1974, 96, 4334-4335.

(40) Milder, S. J.; Goldbeck, R. A.; Kliger, D. S.; Gray, H. B. J. Am. Chem. Soc. 1980, 102, 6761-6764.

(41) Sutton, L. E. (ed.) "Tables of Interatomic Distances and Configuration in Molecules and Ions"; The Chemical Society: London, 1958.

(42) Sheldon, J. C. Nature 1959, 184, 1210-1213.

(43) Strickler, S. J.; Berg, R. A. J. Chem. Phys. 1962, 37, 814-822.

(44) Kettle, S. F. A. Theor. Chim. Acta 1965, 3, 211-212.

(45) Crossman, L. D.; Olsen, D. P.; Duffey, G. H. J. Chem. Phys. 1963, 38, 73-75.

(46) Cotton, F. A.; Haas, T. E. Inorg. Chem. 1964, 3, 10-17.

(47) Guggenberger, L. J.; Sleight, A. W. Inorg. Chem. 1969, 8, 2041-2049.

(48) Briat, B.; Rivoal, J. C.; Kahn, O.; Moreau, S. Chem. Phys. Lett. 1974, 26, 604-606; Briat, B.; Rivoal, J. C.; Kahn, O.; Moreau, S. Proc. Int. Conf. Coord. Chem. 16th 1974, 2.25a.

(49) Cotton, F. A.; Stanley, G. G. Chem. Phys. Lett. 1978, 58, 450-453.

(50) Seifert, G.; Grossmann, G.; Müller, H. J. Mol. Struct. 1980, 64, 93-102.

(51) Seifert, G.; Finster, J.; Müller, H. Chem. Phys. Lett. 1980, 75, 373-377.

(52) Tjabbes, B. Th. Proc. K. Ned. Akad. Wet. 1932, 35, 693-700.

(53) Carmichael, W. M.; Edwards, D. A. J. Inorg. Nucl. Chem. 1967, 29, 1535-1538.

(54) Robbins, D. J.; Thomson, A. J. J. Chem. Soc. Dalton Trans. 1972, 2350-2364.

(55) Fleming, P. B.; McCarley, R. E. Inorg. Chem. 1970, 9, 1347-1354.

(56) Ferguson, J. A.; Meyer, T. J. J. Am. Chem. Soc. 1972, 94, 3409-3412.

(57) See, for example, Holloway, J. D. L.; Geiger, W. E., Jr. J. Am. Chem. Soc. 1979, 101, 2038-2044.

(58) Nicholson, R. S. Anal. Chem. 1966, 38, 1406.

(59) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970.

(60) Webster, O. W.; Mahler, W.; Benson, R. E. J. Am. Chem. Soc. 1962, 84, 3678-3684.

(61) Foster, R.; Thomson, T. J. Trans. Faraday Soc. 1962, 58, 860-868.

(62) Extinction coefficients for $TCNE^-$ (ref. 60) and chloranil$^-$ (ref. 61) have been remeasured: Nocera, D. G.; Gray, H. B. J. Am. Chem. Soc. submitted for publication. For $TCNE^-$ in CH_2Cl_2, $\epsilon_{469} = 4.6 \times 10^3$ M^{-1} cm^{-1}; for chloranil in CH_3CN, $\epsilon_{483} = 2.2 \times 10^3$ M^{-1} cm^{-1}.

(63) Varga, E. M., Jr.; Papaconstantinou, E.; Pope, M. T. Inorg. Chem. 1970, 9, 662-667.

(64) Geoffroy, G. L.; Wrighton, M. S.; Hammond, G. S.; Gray, H. B. J. Am. Chem. Soc. 1974, 96, 3105-3108.

(65) Mann, K. R.; Gordon, J. G., II; Gray, H. B. J. Am. Chem. Soc. 1975, 97, 3553-3555.

(66) Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B. Inorg. Chem. 1978, 17, 828-834.

(67) Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. J. Am. Chem. Soc. 1976, 98, 7461-7463.

(68) Mann, K. R.; Lewis, N. S.; Miskowski, V. M.; Erwin, D. K.; Hammond, G. S.; Gray, H. B. J. Am. Chem. Soc. 1977, 99, 5525-5526.

(69) Gray, H. B.; Miskowski, V. M.; Milder, S. J.; Smith, T. P.; Maverick, A. W.; Buhr, J. D.; Gladfelter, W. L.; Sigal, I. S.; Mann, K. R. Fundam. Res. Homogeneous Catal. [Proc. Int. Workshop] 1979, 3, 819-834.

(70) Miskowski, V. M.; Sigal, I. S.; Mann, K. R.; Gray, H. B.; Milder, S. J.; Hammond, G. S.; Ryason, P. R. J. Am. Chem. Soc. 1979, 101, 4383-4385.

(71) Sigal, I. S.; Mann, K. R.; Gray, H. B. J. Am. Chem. Soc. 1980, 102, 7252-7256.

(72) Sigal, I. S.; Gray, H. B. J. Am. Chem. Soc. 1981, 103, 2220-2225.

(73) Mann, K. R.; DiPierro, M. J.; Gill, T. P. J. Am. Chem. Soc. 1980, 102, 3965-3967.

(74) Milder, S. J. Ph. D. thesis, University of California, Santa Cruz, 1979; Chesick, J. P. unpublished results.

(75) Smith, T. P.; Gray, H. B. Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 24-29, 1980, INOR.

(76) Mann, K. R.; Thich, J. A.; Bell, R. A.; Coyle, C. L.; Gray, H. B. Inorg. Chem. 1980, 19, 2462-2466.

(77) Lewis, N. S. M. S. thesis, California Institute of Technology, 1977.

(78) Sigal, I. S. unpublished results (for methods see ref. 72).

(79) Cooley, R. M.; Yost, D. M. Inorg. Syn. 1946, 2, 69-73.

(80) Lux, H.; Illman, G. Ber. 1958, 91, 2143-2150.

(81) Shimi, I. A. W.; Higginson, W. C. E. J. Chem. Soc. 1958, 260-263.

(82) Stähler, A.; Wirtwein, H. Ber. 1905, 38, 2619-2629.

(83) Rillema, D. P.; Endicott, J. F.; Papaconstantinou, E. Inorg. Chem. 1971, 10, 1739-1746.

(84) Grüniger, H.-R.; Sulzberger, B.; Calzaferri, G. Helv. Chim. Acta 1978, 61, 2375-2380.

(85) Wegner, E. E.; Adamson, A. W. J. Am. Chem. Soc. 1966, 88, 394-404.

(86) Richman, R. M.; Mann, K. R. unpublished results.

(87) Gray, H. B.; Mann, K. R.; Lewis, N. S.; Thich, J. A.; Richman, R. M. Advan. Chem. Ser. 1978, No. 168, 44-56.

(88) Najdzionek, J. S. Ph. D. thesis, California Institute of Technology, 1982.

(89) Dartiguenave, Y.; Dartiguenave, M. unpublished results.

(90) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. J. Am. Chem. Soc. 1979, 101, 1298-1300.

(91) Tait, A. M.; Hoffman, M. Z.; Hayon, E. J. Am. Chem. Soc. 1976, 98, 86-93.

(92) Schugar, H. J.; Hubbard, A. T.; Anson, F. C.; Gray, H. B. J. Am. Chem. Soc. 1969, 91, 71-77.

(93) Burkhart, J. L. (ed.) "Barry's Bible"; Caltech: Pasadena, 1981.

(94) Pecsok, R. L.; Maverick, E. F. J. Am. Chem. Soc. 1954, 76, 358-362.

(95) Anderson, C. P.; Salmon, D. J.; Meyer, T. J.; Young, R. C. J. Am. Chem. Soc. 1977, 99, 1980-1982.

(96) Hellwege, K.-H.; Hellwege, A. M. (eds.) "Landolt-Börnstein"; Springer: Berlin; 6th ed., v. 2, part 10, 1967; New Series, v. 2, part 2, 1966.

(97) Sheldrick, G. M. "SHELX76, a program for crystal structure determination"; Cambridge University, 1976. The program's own scattering factors were used for all atoms other than Rh; the Rh scattering factors were taken from "International Tables for X-Ray Crystallography"; vol. 4; Kynoch Press: Birmingham, 1974.

(98) Johnson, C. K. "ORTEP"; Oak Ridge National Laboratory Report ORNL-3794, 1965.

(99) Mann, K. R.; Bell, R. A.; Gray, H. B. Inorg. Chem. 1979, 18, 2671-2673.

(100) Smith, T. P.; Maverick, E. F. unpublished results.

(101) Mann, K. R. Cryst. Struct. Comm. 1981, 10, 451-457.

(102) Endres, H.; Gottstein, N.; Keller, H. J.; Martin, R.; Rodemer, W.; Steiger, W. Z. Naturforsch. 1979, 34b, 827-833.

(103) Olmstead, M. M.; Balch, A. L. J. Organometall. Chem. 1978, 148, C15-C18. We thank Professor Balch for providing us with the atomic coordinates for this structure and for the one in Ref. 104.

(104) Balch, A. L.; Olmstead, M. M. J. Am. Chem. Soc. 1979, 101, 3128-3129.

PROPOSITIONS

ABSTRACTS

I. The interactions of positronium (Ps) with photoexcited organic and inorganic phosphors are to be studied in the solid state. Attempts will be made in particular to quench the emission of the phosphors by spin conversion of ^3Ps to ^1Ps.

II. The electronic spectra and chemical properties of three pentacarbonylnitrosylmetal (d^6) complexes are to be studied and compared to those of the corresponding unsubstituted hexacarbonyls. Methods for synthesis of the complexes, only one of which has previously been prepared, are proposed.

III. The biosynthesis of fluoroacetate from fluoride is to be investigated. Two possible synthetic schemes are presented and experiments to evaluate these mechanisms are described.

IV. Bis(β-diketone) ligands are to be used to prepare "face-to-face" binuclear metal complexes. These are expected to display redox activity for ligands attached both between the metal atoms and outside them, and should offer extensive opportunities for thermal and photochemical redox reactions of small molecules.

V. Polar guest molecules in clathrates and related inclusion compounds should exhibit partial alignment in strong electric fields. Possible applications of this phenomenon to magnetic resonance, optical and microwave spectra and to stereospecific chemical reactions are discussed.

PROPOSITION I

Luminescence Quenching by Triplet Positronium

Experimental evidence for the existence of positronium (Ps), the bound state of a positron and an electron, was first presented in 1949.[1] Since then the study of the annihilation of positrons and Ps in matter has developed into an important experimental chemical technique. Several reviews[2-5] describe the evolution of positronium chemistry since the early 1950s.

As both e^+ and e^- have spin 1/2, Ps exists in singlet and triplet states, "para-" and "orthopositronium" respectively. The triplet is higher in energy by approximately 0.0008 eV.[6] The lifetime of ^{1}Ps is 0.125 ns in free space, and its annihilation leads to an even number of photons (nearly always two). Since the triplet must produce an odd number of photons, usually 3, its lifetime is longer (140 ns in free space).

In a typical positronium experiment positrons are given off by a radioisotope (e.g. ^{22}Na, ^{64}Cu), enter the sample and lose energy in collisions with the sample. The formation of positronium may occur as follows:

$$e^+ + X = Ps + X^+, \qquad (1)$$

where X is some atom in the sample.[7] The so-called "Ore gap" theory predicts that reaction (1) will be irreversible only for a narrow range of positron energies. As the entering positron slows down, then, it may capture an electron to make Ps; or if it loses too much energy it can

only annihilate. Annihilation is most probable at very low e^+ energies, so that the actual fraction of positrons appearing as Ps may be as high as 50%.

The experiments normally employ a delayed-coincidence apparatus, which measures the delay between emission and annihilation of individual positrons. A graph of the number of annihilations against decay time therefore shows both the lifetimes of the two Ps states and the relative amounts of each produced in a given substance. The effects of matter on positrons may be measured, then, in terms of changes in the two lifetimes and in the proportion of ^{3}Ps decays observed. The fraction of ^{3}Ps annihilation observed may be reduced by several methods:

1) pick-off, in which the Ps positron annihilates with an electron in a nearby molecule;
2) oxidation, i.e. chemical removal of the Ps electron by the sample;
3) Ps compound formation, where Ps behaves as a hydrogenlike radical; and
4) spin conversion, according to the equation

$$^3\text{Ps} + {}^m\text{X} = {}^1\text{Ps} + {}^n\text{X}, \qquad (2)$$

where ^{m}X or ^{n}X must represent a paramagnetic species.

Thus for m = 1 (singlet quencher), ^{n}X must represent a triplet; otherwise n may be any nonzero member of the set {m + 2, m, m - 2}. It should be noted that spin conversion of ^{1}Ps to ^{3}Ps is subject to the same spin selection rules. The lifetimes of ^{1}Ps and ^{3}Ps in free space make conversion quenching of the singlet negligible; but in condensed phases, pick-off processes lower the ^{3}Ps lifetime drastically. Under

these conditions[8] the quenching must be regarded as spin equilibration of Ps,

$$^3Ps \overset{X}{\rightleftharpoons} {}^1Ps, \qquad (3)$$

and the measured lifetime tends toward the statistical average of τ_S and τ_T.

Pick-off occurs in all media. Oxidation processes are dependent on the electron affinity of the sample. Ps forms compounds with species known to undergo radical reactions, e.g. Cl_2 and N_2O_4. The last of the four possibilities forms the principal emphasis here: spin conversion will be used as a tool for studying phosphorescence properties of organic and inorganic compounds.

An early example of spin conversion of Ps was in argon - NO mixtures. Small quantities of NO (> 0.1 mol %) in 1 atm of Ar quench ^3Ps at a rate close to the diffusion limit.[9] Quenching by O_2 illustrates the flexibility of the spin correlation rules: the quenching occurs by spin conversion,[10] even though the lowest singlet state of O_2 is energetically inaccessible to ^3Ps.

Studies of ^3Ps quenching in aqueous solution are well summarized by Tao.[5] Paramagnetic metal complexes react rapidly with ^3Ps: for example, the rate constant for quenching by $Fe(H_2O)_6^{2+}$ is 1.4×10^9 M^{-1} s^{-1}, while it is nearly zero for $Fe(CN)_6^{4-}$.

Brandt and co-workers have studied reactions of ^3Ps with paramagnetic organic quenchers, both in the gas phase[11] and in the solid state.[12-15] In the solid-state experiments a solution of an organic phosphor (e.g. naphthalene or chlorophyll) was cooled to make a glass and was placed over a ^{22}Na source. The proportions of ^3Ps and ^1Ps in

the sample were determined using a delayed coincidence apparatus, both in the dark and under illumination from a filtered mercury arc lamp. They measured shorter lifetimes and lower intensities for ^3Ps in the photoexcited samples than in the dark, and concluded that the principal quenching reaction for an organic phosphor G was

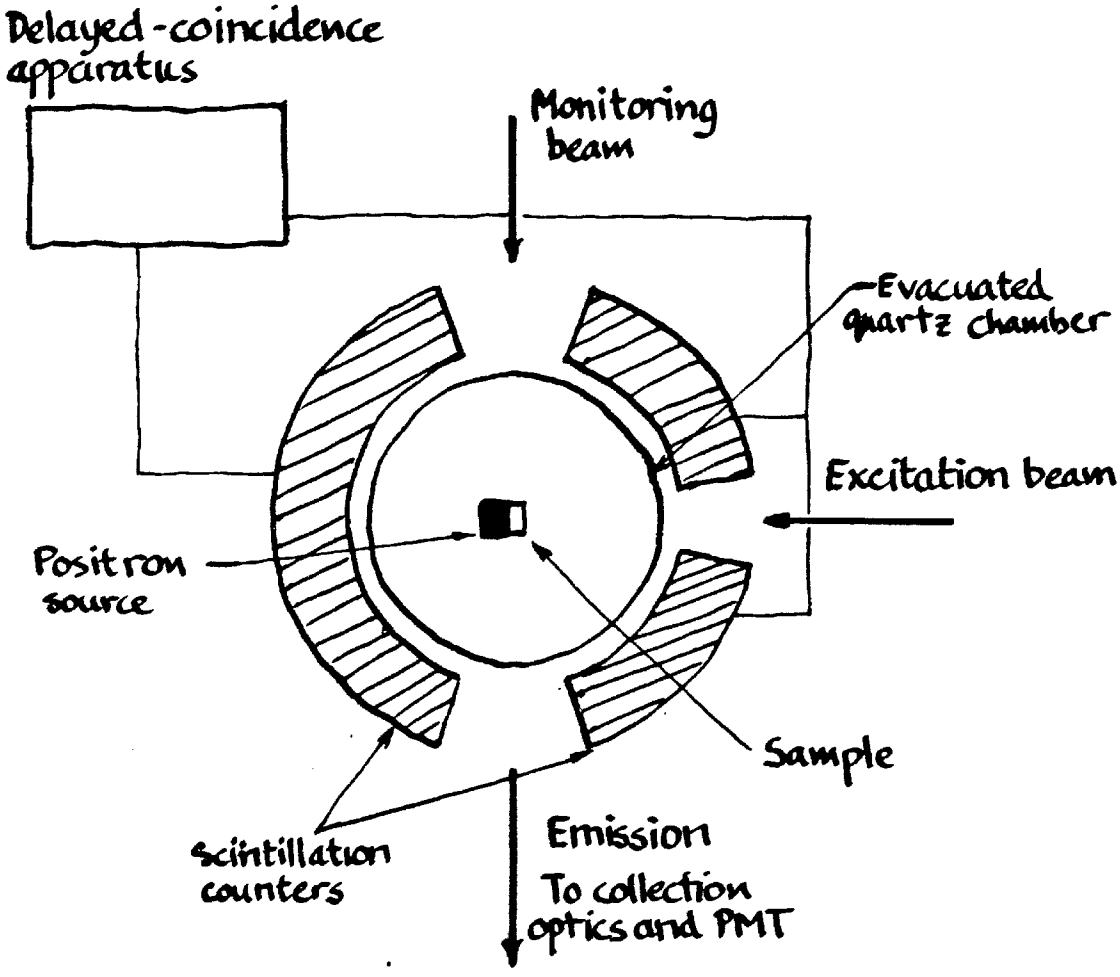
$$^3Ps + {}^3G^* = {}^1Ps + {}^1G. \qquad (4)$$

Although Brandt and co-workers showed that the lifetime of ^3Ps is reduced by photogenerated triplet states, they did not look for changes in luminescence intensity. It is proposed here to examine the effects of positronium spin conversion on the luminescence of the compounds, and to extend the studies to reactions with excited states of transition metal complexes.

The apparatus to be used would be based on that of Brandt et al.,[13] with modifications, as in Figure 1. It contains a crystal of the sample attached to a positron source (and to a cryostat for work at low temperature). The decay and annihilation gamma rays are detected in the two scintillation counters and analyzed by the delayed-coincidence unit. The addition of emission and transient absorption facilities would allow the detection of spin conversion in a new manner. The experiments would proceed in a straightforward fashion, correlating the delayed-coincidence measurements of changes in ^3Ps lifetime with the changes in emission intensity and lifetime. Transient absorption spectra would also be useful in monitoring excited state concentrations in the sample in the presence and absence of Ps.

Two specific problems arise in carrying out this type of experiment: the overall fraction of excited states that will react with Ps,

Figure 1. Apparatus for measurement of ^3Ps spin conversion and crystal luminescence.


Delayed-coincidence apparatus
Monitoring beam
Evacuated quartz chamber
Excitation beam
Positron source
Sample
Scintillation counters
Emission
To collection optics and PMT

and interference from the Ps formation process itself. The first difficulty is due to the relatively low intensity of radioisotope e^+ sources and to the low efficiency of Ps formation from fast positrons. It can be overcome by using an accelerator as a source of e^+ [16] and a moderator system[17,18] to increase the yield of Ps from positrons. Here the optical detection of Ps spin conversion removes the requirement inherent in delayed-coincidence apparatus that the emission of the positrons from the source be individually detectable. In the second case Aravin and co-workers[19] report that the luminescence intensity of anthracene is decreased in the "spurs" left by high-energy positrons as they make Ps. This would also be solved by the use of the MgO moderator,[18] which would allow generation of thermal Ps outside the sample.

The apparatus described here could in principle be used with any phosphor, and offers several advantages over classical methods[20,21] for the study of energy transfer. First, energy transfer has generally been examined in fluid solution. Especially with metal complexes, this limits severely the variety of possible substrates. The use of Ps, however, by virtue of its lightness and rapid diffusion, makes experiments easy even in the solid state at low temperature. Second, the experiments proposed will allow for direct comparison of the "spin-flip" and "exchange" processes described by Brandt.[14] Only the exchange mechanism is allowed for a ground-state conversion quencher such as O_2; but for excited states both processes can occur. Also, it is possible that ^3Ps, if formed with excess kinetic energy, could cause phosphorescence even in the absence of an exciting beam. And finally, the facilities for transient absorption spectra will enable Ps oxidation and compound formation to be evaluated directly as competitors with spin conversion.

Spin conversion of ^3Ps by molecular excited states could be used in a systematic study of emissive properties of these substrates. Ps is neutral and therefore its reactions are expected to be independent of electrostatic forces. And as a single, versatile donor it eliminates the need to consider donor properties in comparisons of quenching rates. The study might lead to generalizations both about the relative energies of the various excited states and about the spin-conversion process in general.

References

(1) Shearer, J. W.; Deutsch, M. Phys. Rev. 1949, 76, 462.

(2) Green, J. H.; Lee, J. "Positronium Chemistry"; Academic Press: New York, 1964.

(3) Merrigan, J. A.; Green, J. H.; Tao, S.-J. "Techniques of Chemistry"; Weissberger, A.; Rossiter, B. (eds.), vol. I, part IIID, Wiley-Interscience: New York, 1972, pp 502-586.

(4) Gol'danskii, V. I.; Shantarovich, V. P. "Modern Physics in Chemistry"; Fluck, E.; Gol'danskii, V. I. (eds.), vol. I, Academic Press: New York, 1976, pp 269-308.

(5) Ache, H. J., Jr. Advan. Chem. Ser. 1979, No. 175, 1-49.

(6) Deutsch, M.; Brown, S. C. Phys. Rev. 1952, 85, 1047-1048.

(7) See, for example, Tao, S.-J. Appl. Phys. 1976, 10, 67-79.

(8) West, R. N. J. Phys. Chem. 1980, 84, 1286-94.

(9) Heinberg, M.; Page, L. A. Phys. Rev. 1957, 107, 1589-1600.

(10) Klobuchar, R. L.; Karol, P. J. J. Phys. Chem. 1980, 84, 483-488.

(11) Brandt, W.; Spektor, D. Phys. Rev. Lett. 1977, 38, 595-599.

(12) Brandt, W.; Kliauga, P. Phys. Rev. Lett. 1973, 30, 354-357.

(13) Brandt, W.; Kliauga, P. Phys. Rev. B 1976, 14, 884-895.

(14) Brandt, W. Appl. Phys. 1974, 5, 1-23.

(15) Brandt, W. Advan. Chem. Ser. 1979, No. 175, 89-107.

(16) Stein, T. S.; Kauppila, W. E.; Roellig, L. O. Rev. Sci. Instrum. 1974, 45, 951-953.

(17) Mills, A. P., Jr. Appl. Phys. 1980, 23, 189-191.

(18) Griffith, T. C.; Heyland, G. R.; Lines, K. S.; Twomey, T. R. Phys. Lett. A 1978, 69, 169-171.

(19) Aravin, L. G.; Gol'danskii, V. I.; Filimonov, M. K.; Shantarovich, V. P. Khim. Vys. Energ. 1980, 14, 188-190; see C. A. 1980, 92, 187515m.

(20) Lamola, A. A. "Techniques of Organic Chemistry"; Leermakers, P. A.; Weissberger, A. (eds.), vol. XIV, Interscience: New York, 1969, Ch. II.

(21) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. Coord. Chem. Rev. 1975, 15, 321-433.

PROPOSITION II

Pentacarbonylnitrosylmetal Complexes

Nitric oxide occupies a unique position among transition metal ligands. Its so-called "non-innocent" behavior has inspired a number of theoretical studies[1-5] concerning electronic configuration and modes of coordination. It can act as a very strong π acceptor, forming complexes that in some cases are nearly inert to substitution. On the other hand, coordinated NO has been shown to participate directly in a number of chemical reactions.[6,7] Yet few systematic experimental studies of the electronic properties of nitrosyl complexes have been undertaken.

The electronic structures and spectra of octahedral complexes of CO and CN^- have been examined;[8,9] these studies form the basis for much of the theoretical interpretation of their photochemistry (see, for example, Refs. 10 and 11). A similar investigation[12] reports on the properties of pentacyanonitrosylmetalates. In these complexes the principal effect of the NO ligand was found to be the introduction of low-lying unoccupied MOs having partial π^* (NO) character. The lowest energy spin-allowed bands in the electronic spectra were therefore interpreted as MLCT. The proposed study offers an opportunity to examine the effects of the NO ligand on the properties of another series of π-acceptor complexes. In particular, the complexes $(CO)_5CrNO^+$ and $(CO)_5MnNO^{2+}$ are to be prepared and their properties compared to those of the known, isoelectronic $(CO)_5VNO$.

Only a few complexes containing exclusively CO and NO as ligands have been reported. Most of these fall into two series:[1] the pseu-

dotetrahedral complexes, isoelectronic with $Ni(CO)_4$, and the five-coordinate species similarly derived from $Fe(CO)_5$. The proposed treatment of the octahedral complexes would offer two advantages over that of the known series. First, the corresponding hexacarbonyls are well characterized and information about their electronic structure is available from both spectroscopic and photochemical sources. Second, reactions of octahedral complexes are often more easily studied than those of five-coordinate and tetrahedral species.

The synthesis of $(CO)_5VNO$ was first reported in 1961 by Hieber and co-workers,[13] who obtained it as a red-violet solution on passage of NO through a solution of $V(CO)_6$ in cyclohexane. Heating the solution or adding excess NO appeared to cause decomposition. The complex has since been isolated in pure form,[14] but has not been described otherwise. The isoelectronic species $(CO)_5CrNO^+$ and $(CO)_5MnNO^{2+}$ might be prepared by one of two general methods:

1) Displacement of a weakly coordinated ligand by NO^+ from $NOPF_6$: likely candidates for this reaction include $(CO)_5Cr(THF)$,[15] $(CO)_5Mn(NCCH_3)^+$ [16] and $(CO)_5MnOClO_3$.[17]

2) Reaction of a 17-electron species with NO (as in the original preparation of the vanadium complex). $Cr(CO)_6^+$ has been prepared by anodic oxidation of $Cr(CO)_6$ in acetonitrile;[18] and complexes of Mn^{2+} with poorly coordinating ligands, such as CH_3CN and DMSO, are known.[19,20]

The principal features of the electronic spectra of the pentacarbonylnitrosyls may be predicted from the simplified MO diagram in

Figure 1. For the d^6 complexes, $(e)^4(b_2)^2$, the lowest energy spin-allowed transitions should be $b_2 \rightarrow \pi^*$ (NO) and $d\pi \rightarrow \pi^*$ (NO). Close to the second of these in energy should be the first two d-d bands, both orbitally forbidden; and somewhat higher, the first orbitally allowed d-d transition, $xz,yz \rightarrow z^2$ ($^1A_1 \rightarrow {}^1E$). This last transition is likely to be obscured by the metal-CO charge transfer bands. In general, then, the hexacarbonyl spectra are expected to serve as a good guide for the pentacarbonylnitrosyl compounds, with the exception of the two low-energy M - NO CT bands.

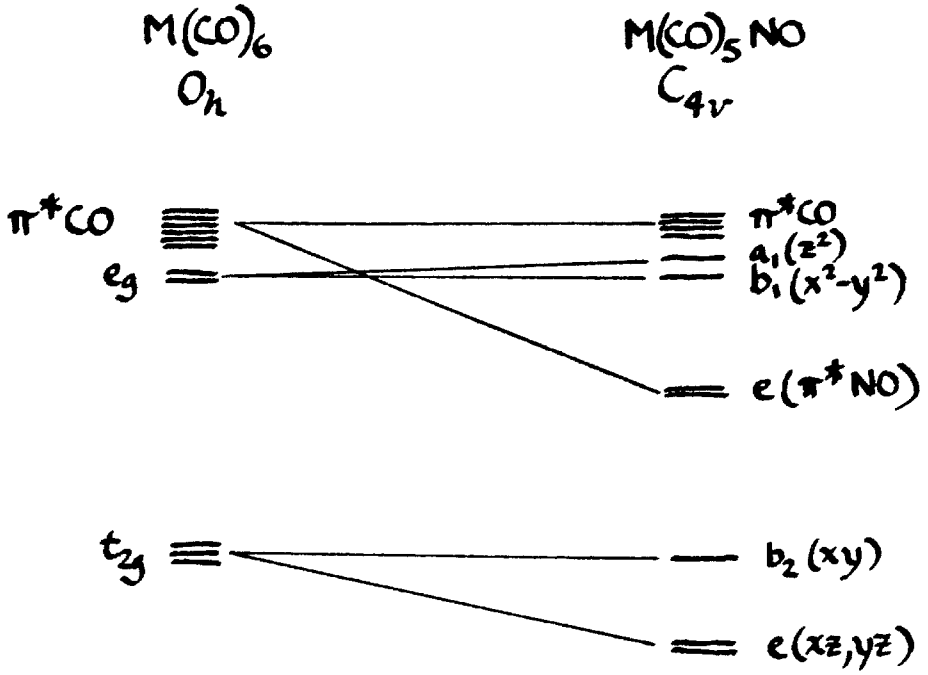
The qualitative MO scheme depicted here could be evaluated with the proposed complexes. Additional information concerning the bonding in the complexes might be obtained from studies of the relative nucleophilicities of the CO and NO ligands, from photochemical reactions, and from redox reactions at NO. Several specific experiments would be of interest with respect to the spectroscopic features of the complexes.

1) $Re(CO)_6^+$ exchanges oxygen with solvent water even in acidic solution, whereas $Mo(CO)_6$ is unaffected.[21] Similar experiments would be conducted with the carbonylnitrosyls, looking for differences in reaction rates among the NO and cis and trans CO ligands.

2) The electrochemistry of $Fe(CN)_5NO^{2-}$, the best known of all nitrosyl complexes, has been the subject of some controversy.[7] A recent study of this ion in nonaqueous solution[22] demonstrated a relatively simple system of complexes, and I would conduct comparable experiments with the proposed complexes.

The nature of the acceptor orbital suggests the possibility of inducing stereochemical change on reduction, for example

Figure 1. Qualitative MO diagram for hexacarbonylmetal and pentacarbonylnitrosylmetal species.


M(CO)6
Oh
M(CO)5NO
C4v
π*CO
eg
π*CO
a1(z2)
b1(x2-y2)
e(π*NO)
t2g
b2(xy)
e(xz,yz)

$$(CO)_5MnNO^{2+} + 2\ e^- = (CO)_4MnNO, \qquad (1)$$

a reaction which might proceed via a bent-NO $(CO)_5MnNO$ intermediate.

Radicals produced as intermediates in these reductions could be characterized by classical methods and by their independent generation in photochemical electron transfer reactions.

3) The effects of the $(CO)_5M$ "substituent" on the properties of NO could also be examined through condensations with amines. Among the amines expected to condense with these nitrosylcarbonyls are metal-ammine complexes such as $Ru(NH_3)_6^{3+}$, perhaps forming asymmetrical N_2-bridged binuclear species, e.g. $(CO)_5Cr-N{\equiv}N-Ru(NH_3)_5^{2+}$ (compare the formation of $[(NH_3)_5Ru]_2N_2^{4+}$ from $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_5NO^{3+}$ [23]). The isolation of such a complex would represent the stabilization of the $(CO)_5CrN_2$ moiety by coordination to a second metal atom.

The proposed study offers an opportunity to examine a series of simple NO complexes and to compare them with known classes of nitrosyls in terms of their spectroscopic, photochemical and redox properties. They are expected to provide not only an advance in fundamental investigations of metal complexes but also further insight into the electronic structure and reactivity of coordinated nitric oxide.

References

(1) Enemark, J. H.; Feltham, R. D. Coord. Chem. Rev. 1974, 13, 339-406.

(2) Eisenberg, R.; Meyer, C. D. Accounts Chem. Res. 1975, 8, 26-34.

(3) Hoffman, R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. Inorg. Chem. 1974, 13, 2666-2675.

(4) Jensen, J. R.; Fenske, R. F. Theor. Chim. Acta 1978, 48, 241-249.

(5) Bottomley, F.; Grein, F. J. Chem. Soc. Dalton Trans. 1980, 1359-1367.

(6) Bottomley, F. Accounts Chem. Res. 1978, 11, 158-163.

(7) McCleverty, J. A. Chem. Rev. 1979, 79, 53-76.

(8) Gray, H. B.; Beach, N. A. J. Am. Chem. Soc. 1963, 85, 2922-2927.

(9) Beach, N. A.; Gray, H. B. J. Am. Chem. Soc. 1968, 90, 5713-5721.

(10) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: London, 1970.

(11) Wrighton, M. S. Chem. Rev. 1974, 74, 401-430.

(12) Manoharan, P. T.; Gray, H. B. Inorg. Chem. 1966, 5, 823-839.

(13) Hieber, W.; Peterhans, J.; Winter, E. Ber. 1961, 94, 2572-2578.

(14) French Patent 1,322,168; C. A. 1964, 60, P3015c.

(15) Strohmeier, W. Angew. Chem. Int. Ed. Engl. 1964, 3, 730-735.

(16) Drew, D.; Darensbourg, D. J.; Darensbourg, M. Y. Inorg. Chem. 1975, 14, 1579-1584.

(17) Wimmer, F. L.; Snow, M. R. Austral. J. Chem. 1978, 31, 267-278.

(18) Pickett, C. J.; Pletcher, D. J. Chem. Soc. Dalton Trans. 1975, 879-886.

(19) Chan, S. I.; Fung, B. M.; Lütje, H. J. Chem. Phys. 1967, 47,

2121-2130.

(20) Selbin, J.; Bull, W. E.; Holmes, L. H., Jr. J. Inorg. Nucl. Chem. 1961, 16, 219-224.

(21) Muetterties, E. L. Inorg. Chem. 1965, 4, 1841-1842.

(22) Bowden, W. L.; Bonnar, P.; Brown, D. B.; Geiger, W. E., Jr. Inorg. Chem. 1977, 16, 41-43.

(23) Guengerich, C. P.; Schug, K. Inorg. Chem. 1978, 17, 1378-1379.

PROPOSITION III

Biosynthesis of Fluoroacetate

The presence of fluoroacetate as a toxic component of certain South African plants was first shown in 1943.[1] Since then six other organofluorine compounds have been found to occur naturally: four ω-fluorocarboxylic acids,[2,3] the antibiotic nucleocidin (a derivative of adenosine),[4] and fluoroacetone.[5] While it is known that fluoride can be taken up by these plants and converted to fluoroacetate,[1,6-8] a definite biosynthetic pathway has not been demonstrated.

The plants which produce fluoroacetate and the other fluoroacids are frequently toxic to animals. The toxic action of these fluorinated compounds has been traced[9] to their conversion to fluorocitrate, which inhibits the enzyme aconitase in the citric acid cycle.[10,11] A study of the formation of fluoroacetate would be of interest for two reasons. Knowledge of the pathway might suggest means for suppressing the toxicity of fluoroacetate-bearing plants. Also, information might be gained about the effects of fluorinated substrate molecules on enzymes and about the nature of the substrate-enzyme interaction. The size and chemical activity of F are close to those of H, while its electronic properties are more similar to those of OH; thus the role of fluorine substituents in enzymatic processes is not immediately clear.[12]

Three different biosynthetic schemes have been proposed for fluoroacetate. Peters[1] offers the addition or substitution of HF at ethylene as a possible route, but no further work bears on this mechanism. Second, a recent paper suggests that H_2O_2 might cause oxidative

fluorination of malonate to give CO_2 and fluoroacetate,[13] in analogy with the known activity of chloride peroxidase.[14] Also unconfirmed is the hypothesis of Mead and Segal,[15] who suggest that an amino acid, activated by condensation with pyridoxal phosphate, undergoes nucleophilic attack by F^- and subsequent degradation to fluoroacetate. I shall concentrate here on an experimental evaluation of the third mechanism (illustrated in Figure 1) and on an alternative mechanism to be discussed further below.

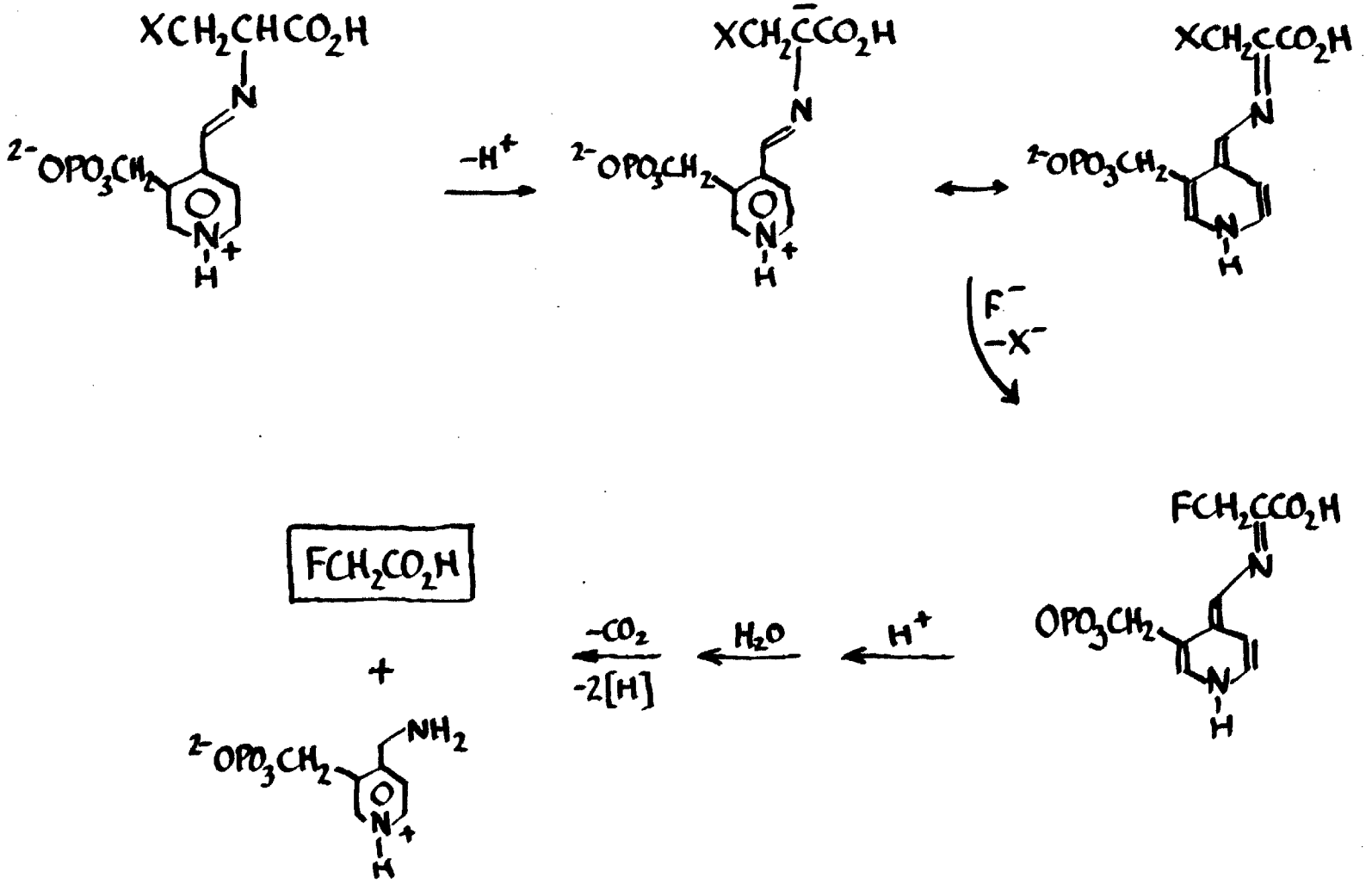
All of the suggested routes to fluoroacetate require the preferential substitution of fluoride as a nucleophile. Standard free-energy tables, however, suggest that nearly all nucleophiles are thermodynamically favored over F^- and HF.[16,17] A few examples follow for derivatives of ethane.

	ΔG°_{298}/kcal mol^{-1}	
$C_2H_5F_{(g)} + H_2O_{(\ell)} = C_2H_5OH_{(\ell)} + HF_{(aq)}$	- 0.93	(1)
$C_2H_5F_{(g)} + HCN_{(aq)} = C_2H_5CN_{(\ell)} + HF_{(aq)}$	-21.49	(2)
$C_2H_{4(g)} + HF_{(aq)} = C_2H_5F_{(g)}$	- 0.28	(3)
$C_2H_{4(g)} + CH_3COOH_{(\ell)} = C_2H_5OOCCH_{3(\ell)}$	- 2.74	(4)

That these ΔG° values should be similar to those for the corresponding amino acid derivatives is illustrated by the following comparison:

$C_2H_5OH_{(\ell)} + H_2S_{(aq)} = C_2H_5SH_{(\ell)} + H_2O_{(\ell)}$	- 9.88	(5)
$HOCH_2CH(NH_2)CO_2H_{(s)} + H_2S_{(aq)} = HSCH_2CH(NH_2)CO_2H_{(s)} + H_2O_{(\ell)}$	-10.66	(6)

Figure 1. Proposed synthesis for fluoroacetate from β-substituted alanine. From ref. 15.


XCH2CHCO2H
N
2-OPO3CH2
N+
H
-H+
XCH2CCO2H
F-
-X-
FCH2CCO2H
OPO3CH2
H+
H2O
-CO2
-2[H]
FCH2CO2H
+
NH2

If the biosynthesis of fluoroacetate is to be accomplished by substitution, then, energy must be added. The hydrolysis of organic phosphates frequently supplies such energy in biological systems. This can take place indirectly, in which case the partial hydrolysis of ATP (for example) drives the desired reaction via an enzyme, or directly, whereby the substrate is converted into a phosphate ester before the desired reaction occurs. Lehninger[18] estimates that the hydrolysis of a phosphate ester results in a free-energy change of -3 to -4 kcal mol^{-1}. Then ΔG^{o} for the reaction

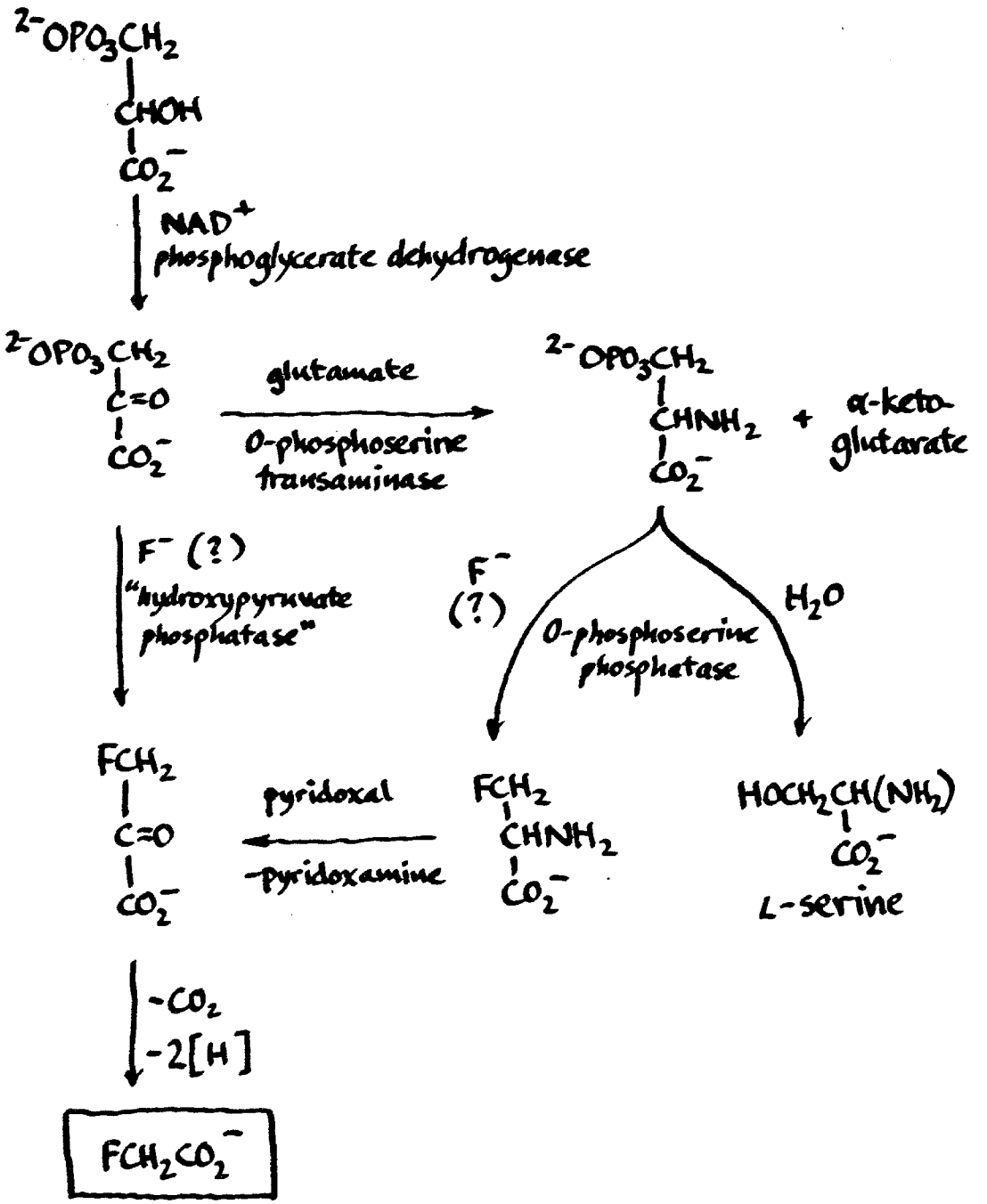
$$C_2H_5OPO_3^{2-}{}_{(aq)} + HF_{(aq)} = C_2H_5F_{(g)} + HPO_4^{2-}{}_{(aq)} \qquad (7)$$

should be negative (perhaps -2 to -3 kcal mol^{-1}). This type of reaction could serve as the basis for Mead and Segal's pyridoxal-assisted fluoroacetate biosynthesis or for a slightly different mechanism not requiring pyridoxal for the substitution.

The biosynthesis of serine involves intermediates of the type shown in Figure 2. Phosphoglycerate dehydrogenase catalyzes the oxidation of 3-phosphoglycerate to O-phosphohydroxypyruvate, which is in turn transaminated by glutamate to give O-phosphoserine and, ultimately, serine. The replacement of phosphate by fluoride in any of the O-phospho derivatives could yield fluoroacetate. Two such reactions are shown. In both cases a phosphatase must allow F^- to enter as nucleophile instead of water. Several experiments might be conducted to evaluate these possible routes:

1) Allow O-phosphoserine phosphatase to act on O-phosphoserine in vitro in the presence of fluoride. It might be necessary in this case

Figure 2. Biosynthesis of serine and its possible relationship to fluoroacetate.


2-OPO3CH2
CHOH
CO2-
NAD+
phosphoglycerate dehydrogenase
2-OPO3CH2
C=O
CO2-
glutamate
O-phosphoserine transaminase
2-OPO3CH2
CHNH2
CO2-
+ α-keto-glutarate
F- (?)
"hydroxypyruvate phosphatase"
F- (?)
H2O
O-phosphoserine phosphatase
FCH2
C=O
CO2-
pyridoxal
-pyridoxamine
FCH2
CHNH2
CO2-
HOCH2CH(NH2)
CO2-
L-serine
-CO2
-2[H]
FCH2CO2-

to isolate the enzyme from a plant known to synthesize fluoroacetate, as the secondary activity of the enzyme in different organisms is expected to vary. For example, Mead and Segal studied the metabolism of cysteine in a plant species that sometimes contains fluoroacetate.[19] Although they observed no uptake of F^- in their study, the seedlings were taken from an area where the species is not observed to produce fluoroacetate!

Alternatively, 2- or 3-^{14}C-O-phosphoserine can be administered to tissue homogenates of appropriate plant species. This would best be done in the absence of glutamate and α-ketoglutarate, thereby preventing normal production of O-phosphoserine. The appearance of 1- or 2-^{14}C-fluoroacetate would support the proposed mechanism.

2) Search for evidence of an enzyme hydrolyzing O-phosphohydroxypyruvate directly ("hydroxypyruvate phosphatase" in Fig. 2). A plant homogenate, after removal of glutamate and α-ketoglutarate to inhibit transamination, could be treated with 2- or 3-^{14}C-O-phosphohydroxypyruvate and F^-. The appearance of radioactive fluoroacetate would be a positive result, as above. The new enzyme might well require F^- as a nucleophile, since there would be little metabolic use for hydroxypyruvate or other possible substitution products.

References

(1) Peters, R. A. "Carbon-Fluorine Compounds: Chemistry, Biochemistry and Biological Activities"; Ciba Found. Symp.; Elsevier: New York, 1972, pp 1-26, 55-70.

(2) Peters, R. A.; Hall, R. J.; Ward, P. F. V.; Sheppard, N. Biochem. J. 1960, 77, 17-23.

(3) Ward, P. F. V.; Hall, R. J.; Peters, R. A. Nature 1964, 201, 611-612.

(4) Morton, G. O.; Lancaster, J. E.; VanLear, G. E.; Fulmore, W.; Meyer, W. E. J. Am. Chem. Soc. 1969, 91, 1535-1537.

(5) Fluoroacetone was produced in plant homogenates: Peters, R. A.; Shorthouse, M. Nature 1971, 231, 123-124.

(6) Peters, R. A.; Shorthouse, M. Phytochem. 1972, 11, 1337-1338.

(7) Weinstein, L. H.; McCune, D. C.; Mancini, J. F.; Colavito, L. H.; Silberman, D. H.; van Leuken, P. Environ. Res. 1972, 5, 393-408.

(8) Vickery, B.; Vickery, M. L. Phytochem. 1975, 14, 423-427.

(9) Peters, R. A.; Buffa, P.; Wakelin, R. W.; Thomas, Proc. Roy. Soc. B 1953, 140, 497-507.

(10) Peters, R. A. Biochem. J. 1961, 79, 261-268.

(11) Glusker, J. P. "The Enzymes"; Boyer, P. D. (ed.); 3rd ed., vol. 5, Academic Press: New York, 1971, ch. 14.

(12) See, for example, Taylor, N. F. "Carbon-Fluorine Compounds: Chemistry, Biochemistry and Biological Activities"; Ciba Found. Symp.; Elsevier: New York, 1972, pp 215-235; Goldman, P. Science 1969, 164, 1123-1130.

(13) Vickery, B.; Vickery, M. L. Experientia 1979, 35, 299-300.

(14) Hewson, W. D.; Hager, L. P. "The Porphyrins"; Dolphin, D. (ed.); v. 6, Academic Press: New York, 1979, pp 295-332.

(15) Mead, R. J.; Segal, W. Austral. J. Biol. Sci. 1972, 25, 327-333.

(16) "Selected Values of Chemical Thermodynamic Properties"; Circular No. 500, National Bureau of Standards: Washington, D. C., 1950.

(17) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.

(18) Lehninger, A. L. "Biochemistry"; 2nd Ed., Worth: New York, 1975.

(19) Mead, R. J.; Segal, W. Phytochem. 1973, 12, 1977-1981.

PROPOSITION IV

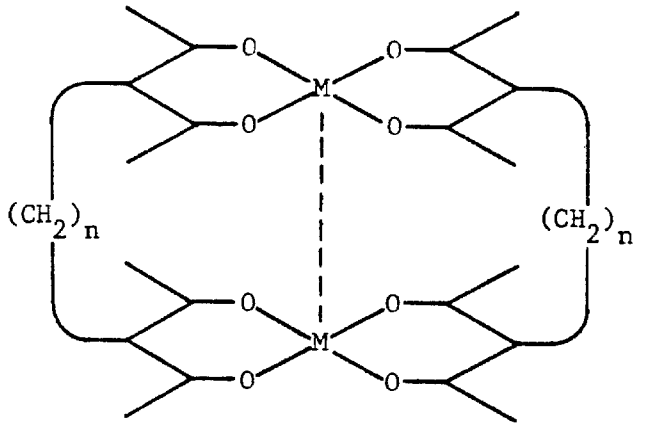
Binuclear Metal Complexes for Redox Reactions of Coordinated Ligands

Common industrial and biological redox reactions nearly always involve the ultimate transfer of several electrons in a single molecule. Metal complexes that promote such reactions in a catalytic fashion are rare, and most redox photochemistry has centered on one-electron processes. The experiments proposed here will explore the spectroscopic and redox processes of a series of new metal complexes, and will use them to attack the problem of multielectron redox catalysis by means of simultaneous redox transformations at the metals and the coordinated ligands. These binuclear complexes will be based initially on bis(β-diketone) ligands, which would bind the two metal atoms in a "face-to-face" geometry as shown in Figure 1(a).

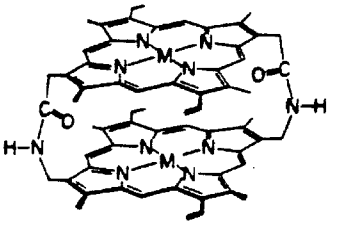
Several other reports discuss binuclear complexes with the same "face-to-face" configuration. Collman and co-workers have explored systems based on two metalloporphyrins joined by amide linkages.[1] One such complex is illustrated in Figure 1(b). On the other hand, Lehn's studies began with cryptates, polycyclic multidentate ligands containing O, N and S donors. Recently he has discussed the use of larger members of the cryptate class in the preparation of binuclear complexes, shown schematically in Figure 1(c).[2] I shall begin by discussing briefly synthetic methods for the proposed complexes, and then compare their projected properties with those of the porphyrin and cryptate systems.

Several of the bis(β-diketone) ligands are described in a paper by Martin and co-workers.[3] These are the n = 6 and n = 10 ligands (see

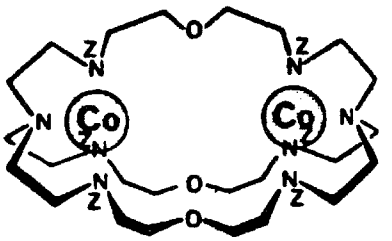
Figure 1. Binuclear metal complexes: (a) Proposed bis(β-diketone) complex; (b) "Face-to-face" porphyrin; (c) binuclear cryptate. See text for references.


O
M
O
O
O
O
O
O
M
O
O
O
$(CH_2)_n$
$(CH_2)_n$

(a)


N
M
N
N
N
O
C
N-H
C
O
H-N
N
M
N
N
N

(b)


O
N
N
Co
Co
N
N
N
N
O
O
N
N

(c)

Figure 1(a)), and the derivative with a bridging CH_2-p-C_6H_4-CH_2 group. Alkylation of acetylacetone and related compounds at activated C-H bonds has been well studied; other members of the series could probably be prepared by the method of ref. 1 or via tetrabutylammonium acetylacetonate.[4] The preparation of the binuclear complexes would be based on standard methods for β-diketone complexes, except that conditions of high dilution (as in ref. 1 and in the ligand synthesis outlined in ref. 2) might be necessary to limit polymer formation.

Complexes with nitrogen coordinated to the metal atoms instead of oxygen would give different ligand environments. These might be prepared via oximes as starting ligands or by carrying out template condensations of the O-bound binuclear complexes with diamines. An additional possibility is that suitably substituted mononuclear macrocyclic complexes[5] could be coupled to form binuclear species with similar bridges.

Two major degrees of freedom are available in designing the complexes of Fig. 1(a). First, variation in n will allow for different types of redox activity between two extremes. Long bridging groups would make possible the insertion of small molecules (e.g. O_2, N_2H_4) and subsequent redox reactions mediated at the metal centers. For smaller values of n, direct metal-metal bonds could form and two-center reactions external to the metal atoms could take place. And second, the use of oximes or macrocyclic condensation products as ligands would provide variation in ligand field strength and redox potentials. Such variation would be useful in controlling the types of redox reactions expected in individual complexes.

If the bridging group is short (n = 3, for example), the complexes should display evidence of direct metal-metal interaction. In the first transition series Co(II) and Cu(II) are often weakly coupled in such environments. A nickel complex of an unsaturated macrocyclic ligand undergoes oxidation to give a dimer with a metal-metal bond;[6] and although the ligands also appear strongly attracted to each other in this case, similar features might be found with the proposed bis(β-diketone) ligands. In the second and third rows, however, the interactions should be much stronger: in related rhodium complexes, for example, solid $Rh(CO)_2(acac)$ is based on an infinite-chain structure,[7] and in $Rh_2(O_2CCH_3)_4$[8] there is a strong metal-metal bond. The complexes proposed here might undergo oxidative addition and reductive elimination reactions, as has been observed in a number of binuclear isocyanide complexes.

As the bridging groups become longer, direct interactions should grow weaker (although it is possible that conformational changes in the ligands would allow short metal-metal distances even for relatively large n). In the extreme case the complex would behave as two monomeric species. But for intermediate sizes of bridging ligand, the opportunity should arise for ligand insertion between the two metal atoms. The flexibility in synthesis of these complexes should allow for two types of control over their participation in redox reactions: not only does the size of the cavity between the metal atoms govern which molecules are likely to insert, it also affects the thermodynamics associated with their redox reactions.

An initial experiment would be directed toward the complex of Fig. 1(a) for M = Co(II) and n = 6, and its reaction with O_2 to give the

corresponding μ-peroxodicobalt(III) complex. Such a reaction, demonstrating the principle of insertion and reduction of small molecules, would be related to experiments with the porphyrins of Fig. 1(b).[1] In addition, though, it would be representative of the versatility of the complexes in redox reactions of small molecules. The complexes might also be used, for example, to promote redox equilibria involving ammonia and hydrazine:

$$\overbrace{\text{Co(II)--Co(II)}} + N_2H_4 \rightleftharpoons \overbrace{\text{Co(II)-NH}_2\text{NH}_2\text{-Co(II)}} \underset{\text{base}}{\overset{H^+}{\rightleftharpoons}} \overbrace{\text{Co(III)-NH}_3\ \ H_3\text{N-Co(III)}}$$

In this process the transfer of electrons at the binuclear Co complex would accompany fission of the N-N bond. In similar complexes the formation or rupture of single bonds (as in $C_2O_4^{2-}$ or $HOCH_2CH_2OH$) might also proceed simultaneously with electron transfer at the metal atoms.

As potential mediators for redox reactions the proposed complexes may be compared with the other binuclear species of Figure 1, both of which are active with respect to reduction of O_2. The face-to-face porphyrin derivatives such as 1(b), although durable and catalytically active, are available only in small quantities because their synthesis is relatively complicated. And in the cryptate complex, 1(c), the binding constant for the second cobalt atom is significantly smaller than the first.[9] Also, the cryptates of this type are sterically blocked in the outer axial positions; therefore one of the types of redox activity proposed here is excluded for them. Thus both the porphyrins and the cryptates have disadvantages that are not shared by the proposed β-diketone derivatives.

Several experiments are envisioned for these complexes. First, a variety of small molecules will be explored as possible substrates for

redox activity when inserted between the metal atoms. These thermal reactions will be correlated with data derived from electrochemical studies. As in the study of Martell and co-workers with oxygen complexes,[10] the variations in redox potentials and in following chemical reactions will be studied. Of greater interest, however, will be the relationship between redox properties and the size of the cavity between the metal atoms. The length of the bridging ligand should have an important influence on thermodynamics for both insertion and redox reactions, and this should be reflected in the electrode potentials. In analogy with Lehn's comparison of metal binding constants in Fig. 1(c),[9] for example, the insertion of ligands between the metal atoms will be examined as a function of bridging group.

Finally, the photochemical properties of the complexes, particularly for second- and third-row metals and short bridging groups, will be studied. Excited states of the complexes might be more prone to oxidative addition than the corresponding ground states. This tendency could be exploited in the photochemical generation of reactive species such as hydrides and alkyls. Again the versatility of the complexes in terms of geometry and ligand environment should be useful in adapting them to specific redox reactions.

The complexes to be studied are not expected to present great synthetic challenges. Yet they would represent a new class of coordination compounds, and would offer a variety of approaches to thermal and photochemical redox reactions of small molecules. Although similar in some respects to porphyrin and cryptate derivatives currently being studied, the proposed complexes possess distinct advantages with respect to flexibility of ligand environment and structural simplicity. With them it

should be possible to design metal frameworks for controlling the course of simple reactions involving small molecules.

References

(1) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. J. Am. Chem. Soc. 1980, 102, 6027-6036.

(2) Lehn, J.-M. Pure Appl. Chem. 1980, 52, 2441-2459.

(3) Martin, D. F.; Fernelius, W. C.; Shamma, M. J. Am. Chem. Soc. 1959, 81, 130-133.

(4) Brändström, A.; Junggren, U. Acta Chem. Scand. 1969, 23, 3585-3586.

(5) Riley, D. P.; Busch, D. H. Inorg. Synth. 1978, 18, 36-44.

(6) Peng, S.-M.; Goedken, V. L. J. Am. Chem. Soc. 1976, 98, 8500-8510.

(7) Dessent, T. A.; Palmer, R. A.; Horner, S. M. Am. Chem. Soc. Symp. Ser. 1974, No. 5, 301-313; Huq, F.; Skapski, A. C. J. Cryst. Mol. Struct. 1974, 4, 411-418.

(8) Koh, Y. B.; Christoph, G. G. Inorg. Chem. 1979, 18, 1122-1128.

(9) Martell, A. E.; Lehn, J.-M.; Motekaitis, R. J. Proc. Int. Conf. Coord. Chem. 21st 1980, 283.

(10) Harris, W. R.; McLendon, G. L.; Martell, A. E.; Bess, R. C.; Mason, M. Inorg. Chem. 1980, 19, 21-26.

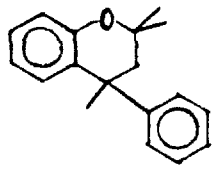
PROPOSITION V

Electric Field Effects on Inclusion Compounds

Inclusion compounds are a class of substances in which a "guest" molecule is enclosed within a fixed structure of "host" molecules. If the cavities formed by the host are two-dimensional the substance is an intercalation compound; if one-dimensional, a channel-type inclusion compound; and if the guest is completely enclosed by the host a clathrate results. Especially in clathrates and also to some extent in channel inclusion compounds, the guest molecules have some rotational freedom of motion. As a result it is often difficult to identify the guest molecule in crystallographic studies: in the hexagonal thiourea channel compound with ferrocene, for example,[1] the cyclopentadienyl rings were fit by an electron density contour with threefold symmetry. Thus these compounds are unusual in that they are well-defined crystalline solids but still allow for significant motion of the guests. If the guest is a polar molecule it should respond to electrostatic forces from an external applied field. I propose to investigate the effects of such external electric fields on the spectroscopic and chemical properties of clathrates and several related compounds.

Recent reviews[2,3] describe various structural and chemical features of inclusion compounds. Urea and thiourea are known to form channel-type compounds, trapping a wide variety of guests in hexagonal channels. Quinol, or hydroquinone, crystallizes with small molecules such as O_2, CH_3OH, and HCN in a clathrate structure with cavities ca. 5 Å in

diameter. When the hosts are larger molecules the cavities can be larger as well: Dianin's compound



was prepared nearly 70 years ago but the clathrate structure of its solvates was not proved for some time. In this structure the cavity is large enough to accommodate 1-heptanol! A number of higher hydrates of small molecules, e.g. $3Br_2.23H_2O$ and $THF.17H_2O$, are actually clathrates as well, with the guests surrounded by cubic arrangements of water molecules.

Thus the clathrates offer a number of different environments for guest molecules. The dynamics of molecular motion within these cavities have been reviewed by Sixou and Dansas.[4] They describe a number of techniques that have been used to monitor the motion of the guests: in general they measure, or at least bracket, the characteristic frequencies as a function of temperature. A discontinuity in heat capacity for a clathrate is sometimes indicative of an order-disorder transition, ad it is often possible to establish that the host undergoes no change. Then the guest molecules are likely to take up specific positions at low temperature and to become disordered on warming. Methods involving IR and NMR spectra, in conjunction with their respective time scales, can also be used to monitor guest motion. Aslaksen suggests[5] that rotational sublevels of vibrational excited states could be used to determine characteristic rotation frequencies for the trapped molecules. However, the direct microwave or far-IR transitions in these substances

are typically rather broad; thus the resolution from such a method may not be good.

Experimental measurements of molecular orientation in electric fields are heavily concentrated on liquid crystals. With smaller molecules there is more controversy: for example, in a recent NMR study of liquid acetonitrile, Plantenga and co-workers established that, in contrast to a previous report, spin-lattice relaxation times were unaffected by electric fields.[6] In more specialized cases, however, there has been some success. An elegant example is the strong electrochromic effects observed for highly polar, long-chain organic dyes in polymers.[7] For a typical molecule with a dipole moment of 1 D, the strongest electric fields commonly accessible (some 10^8 V m^{-1}) lead to a difference in energy between parallel and antiparallel orientation of ca. 0.2 kJ mol^{-1}. In order to measure a significant orientation effect, then, the temperature must be lowered or the dipole moment increased. Clathrates offer an ideal opportunity to make such observations: by extending the temperature range over which reorientation is possible (in the THF-water clathrate, for example, motion of the guest begins just above 20 K[8]), a wide range of molecules should be accessible.

Several types of measurements could be of use with respect to these projected electric field effects. One, mentioned briefly above, is direct microwave absorption. In the gas phase, the orientation of molecular dipoles can often be determined from the Stark effect. However, the breadth of the direct absorptions for clathrates (probably due to the nonuniform potential wells represented by the cavities) makes it unlikely that a small Stark perturbation could be detected. Still, the idea of direct measurement of a molecular dipole moment, particularly

for molecules or ions difficult to vaporize, is intriguing. An additional possibility is that the degree of molecular orientation could be determined from polarization in electronic or vibrational spectra. Finally, "magic angle" solid state NMR spectra are expected to be very useful. The technique has recently been applied to questions of crystallographic order[9] and solid-state fluxionality,[10] and might be appropriate for evaluating close contacts between guests and hosts.

The proposed experiments are expected to have application to the study of clathrates themselves, their guest molecules and related molecules with highly symmetrical structures, and to chemical reactions. Guest molecules in clathrates have naturally favorable positions (especially at low temperature), due to steric factors and intermolecular forces between guest and host as well as to longer-range interactions (e.g. dipole-dipole) among guest molecules. Thus, in the hydroquinone clathrate with acetonitrile, both guest-host and guest-guest interactions are important in determining preferred orientation.[4] The degrees of orientations for various directions of applied electric field could provide information about the shape of the natural cavity potential. One interpretation of such data would be that, for a guest molecule of known dipole moment, its orientation would reflect the local electric field strength within the clathrate cavity. The electric field strength within a solid is normally assumed to be constant everywhere, but clearly these clathrates are microscopically nonuniform. In general, then, the orientations in electric fields will be related to perturbations of local distributions of electric charge. Zeolites, with their highly ionic structures, might be an extreme example of anisotropic charge distributions in the absence of applied fields.

Whereas stretched polymer methods for molecular alignment require geometrical anisotropy, the use of the electric field relies on polarity; thus entirely new groups of compounds could be studied for polarization properties in optical and magnetic resonance spectra. These treatments may be limited by the range of available hosts and host-guest combinations and, therefore, by progress in the synthesis of new clathrates.

As examples of ordinary crystalline materials that may display similar properties in electric fields, the following two are suggested. Sanford and co-workers, in an NMR study of solid solutions of thiophene in benzene,[11] deduced a sixfold potential well for thiophene, which was already known to have substantial rotational freedom. Such wells could probably be modified by electric field methods. In the case of the carboranes (the o-, m- and p-, or 1,2-, 1,7- and 1,12- isomers of dicarba-closododecaborane), the problem is still easier. Here NMR relaxation times showed that these molecules, nearly perfect icosahedra, rotate rapidly in the solid state.[12] Based on measured dipole moments for the three species,[13] p-carborane should be unaffected by an electric field, and o-carborane (μ = 4.5 D) should show a strong effect. The influences of dipole-dipole interactions could be minimized in such a study by doping o-carborane into the "inert" p-carborane.

Finally, the stereospecific polymerization of dienes in thiourea[14] and urea[15] channel-type hosts suggests a new type of experiment. If polar monomers, e.g. 2,3-dichloro-1,4-butadiene or acrylonitrile, were used in such experiments and polymerized while oriented in an electric field at low temperature, corresponding polar polymers might be produced in high yield. Variations in these orientation and polymerization

properties on changing to other channel compounds (such as the cyclotriphosphazenes,[16] whose structure is hexagonal but centrosymmetric) would be studied as well.

Thus a number of new properties of clathrates, concerning both their structure and the molecules inside them, are expected to appear from the proposed study of electric field effects. The experiments represent a new way of orienting molecules for low temperature studies, and should give an additional approach to studying guest-host interactions and the dynamics of guest molecule reorientation. Also, the principles described here can find application to other pure and impure substances with similar rotationally active structures as well as to expanding the range of stereospecific chemical reactions.

References

(1) Hough, E.; Nicholson, D. G. J. Chem. Soc. Dalton Trans. 1978, 15-18.

(2) MacNicol, D. D.; McKendrick, J. J.; Wilson, D. R. Chem. Soc. Rev. 1978, 7, 65-87.

(3) Davies, J. E. D. J. Mol. Struct. 1981, 75, 1-12.

(4) Sixou, P.; Dansas, P. Ber. Bunsenges. Phys. Chem. 1976, 80, 364-389.

(5) Aslaksen, E. W. Phys. Lett. A 1972, 40, 47-48.

(6) Plantenga, T. M.; Lopes Cardozo, H. A.; Bulthuis, J.; MacLean, C. Chem. Phys. Lett. 1981, 81, 223-226.

(7) Van Pelt, P.; Havinga, E. E. "Nonlinear Behaviour of Molecules, Atoms and Ions in Electric, Magnetic or Electromagnetic Fields"; Néel, J. (ed.); Elsevier: Amsterdam, 1979, pp 291-300.

(8) Davidson, D. W.; Garg, S. K.; Ripmeester, J. A. J. Magn. Res. 1978, 31, 399-410.

(9) Shiau, W.-I; Duesler, E. N.; Paul, I. C.; Curtin, D. Y.; Blann, W. G.; Fyfe, C. A. J. Am. Chem. Soc. 1980, 102, 4546-4548.

(10) Lyerla, J. R.; Fyfe, C. A.; Yannoni, C. S. J. Am. Chem. Soc. 1979, 101, 1351-1353.

(11) Sanford, W. E.; Boyd, R. K.; Ripmeester, J. A. Can. J. Chem. 1978, 56, 714-716.

(12) Beckmann, P.; Leffler, A. J. Chem. Phys. 1980, 72, 4600-4607; Beckmann, P.; Wendel, A. J. Chem. Phys. 1980, 73, 3514-3515.

(13) Laubengayer, A. W.; Rysz, W. R. Inorg. Chem. 1965, 4, 1513-1514.

(14) Brown, J. F., Jr.; White, D. M. J. Am. Chem. Soc. 1960, 82,

5671-5678.

(15) White, D. M. J. Am. Chem. Soc. 1960, 82, 5678-5685.

(16) Allcock, H. R. Accounts Chem. Res. 1978, 11, 81-87.